The Hydrogeology of Bromate Contamination in the Hertfordshire Chalk: Incorporating Karst in Predictive Models

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I, Simon James Cook confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

Signed ________________________________

Date ________________________________

Foreword

This Engineering Doctorate (EngD) was funded by an Engineering and Physical Sciences Research Council (EPSRC) Studentship in association with Veolia Water Three Valleys Ltd (VWTV) (Formerly Three Valleys Water Ltd.) and Thames Water Utilities Ltd (TWUL).

As part of the research project two EngD studentships were awarded; 1) to Simon Cook, originator of this document, and 2) to Ciara Fitzpatrick. The research project was intended to be collaborative between the water utilities and University College London with neither individual student affiliated preferentially to either company.

The work documented within this thesis constitutes independent original research, however the research described is complementary to that by Ciara Fitzpatrick in:

> The Hydrogeology of Bromate Contamination in the Hertfordshire Chalk Aquifer: Double-porosity effects on catchment-scale evolution, EngD Thesis, *University College London*, 2010.

The views, opinions and conclusions expressed in the thesis are those of the researcher and do not necessarily reflect the views of Veolia Water Three Valleys Ltd. or Thames Water Utilities Ltd.

Abstract

Point source contamination of groundwater by bromate (BrO_3^-) in the Hertfordshire Chalk Aquifer forced the closure in 2000, of a major public supply groundwater abstraction and presents a continuing threat to regional water resources. Solute transport in the Chalk is dominantly dual porosity in character but in the bromate-affected region of Hertfordshire, karst development along the feather edge of overlying Palaeocene sands and gravels complicates groundwater flow and transport. Tracer tests conducted in the early 20th century indicated rapid (1-3km/day) flow paths of 8-15km in length but a lack of quantitative data has meant that the karst system has not been adequately incorporated into existing models of bromate transport. A new suite of quantitative tracer tests was conducted to investigate the spatial relationship between karst flows and distribution of the bromate contamination, and to establish hydrodynamic transport parameters. Bacteriophage were introduced into the aquifer at 3 locations and their appearance was monitored downgradient. Results indicate that karstification is more widespread than previously indicated. Multiple flow pathways are indicated and evidence of karst penetrating into regions not previously considered karstic. The interpretation has contributed to the development of a new conceptual understanding of the function, geometry and evolution of the Hertfordshire Chalk karst and its influence upon the bromate contamination. Tracer breakthrough analysis suggests a 'dual porosity' exchange between karst conduits and the Chalk matrix, and/or micro-fractures. The analysis enabled determination of transport parameters for incorporation within a regional groundwater flow and transport model.The new conceptual understanding has been incorporated into a spatially distributed groundwater flow and transport model which has been able to reproduce the main features of the karst and transport of the bacteriophage tracers. The model has been applied to simulate bromate transport towards points of interest in the catchment incorporating possible bromate source histories and stresses.

Acknowledgments

Dr William Burgess was my principal supervisor during this project, and I would first and foremost like to express my heartfelt thanks for your guidance and enthusiasm over the past four years. I always came away from our meetings reassured that I was getting it about right, but nonetheless equipped with fresh questions and challenges to take my work forward. I could not have asked for more in a supervisor. I wold also like to thank my secondary supervisor Professor John Barker, not only for introducing me to Willy in the first instance but for opening my mind to considerations and mathematics I would never have considered, nor in the odd case, hope to understand! I would also like to thank Professor Tim Atkinson and Dr Louise Maurice for their guidance and enthusiastic support in the design of my tracer tests.

This Engineering Doctorate was funded by an EngD studentship at UCL and I am grateful to EPSRC, Veolia Water Three Valleys Ltd and Thames Water Utilities Ltd for sponsoring the project. In particular, I would like to thank my supervisors Rob Sage and Lucy Lytton at Veolia Water Three Valleys and Dr Philip Bishop at Thames Water Utilities Ltd. Thank you for all the information advice and feedback you provided and for helping to ground the research in the context of the practical and operational concerns of a Water Utility. I would also especially like to thank you for your help in pulling the right strings with regard to the tracer testing and express my gratitude to all the Veolia Water Three Valleys and Thames Water Utilities Ltd personnel who assisted with sampling and/or access. Particular thanks also go to Jessica Randle at Veolia Water Three Valleys, for providing some of her geophysical data relating to Hertfordshire.

I would also like to thank staff at the Environment Agency, particularly Jon Newton and Jenny Thomas, not only for providing monitoring data but for allowing us to participate in monitoring and in the sharing of other relevant data, including technical reports and a wealth of information relating to swallow hole occurrence. I would also like to thank Jenny Thomas for arranging funding and offering guidance in the design of the tracer testing, it would not have been possible without your assistance.

I am grateful to the many landowners who have allowed me access for mapping and tracer sampling including but not limited to; Lord Salisbury at Hatfield Park, Adrian Sherriff at Nashes Farm and Fairfolds Farm, Adrian Blackwell at Hatfield Quarry and Neil Agnew at Woolmers Park. I would also like to acknowledge Dr John Watkins at CREH analytical, not only for kind advice on bacteriophage but in supplying the tracers and analysis.

The water community at UCL has grown significantly in the past four years and I would like to thank all my fellow researchers for providing a forum in which to discuss, develop and constructively criticise ideas. I am especially grateful to Ciara Fitzpatrick for all her contributions to understanding and progressing research into the bromate contamination and to Mohammed Abdul Hoque for our shared experiences and tips in getting to grips with groundwater modelling in MODFLOW and Argus ONE.

This thesis was typeset using $\LaTeX\,2_\varepsilon$ and I am forever indebted to the many authors of code, packages and tutorials that I have used to create it.

Last but not least I would like to thank my family and especially my wife Sarah, whose overwhelming love and support have kept me going through far too many late nights and early mornings, you might even read this thesis one day! I would also like to thank my dad, Chris Cook and Christine Freeman for offering to proof read parts of this document. Finally I would like to dedicate this thesis to my Grandmother Ruby Cook, I finally "sorted that water out".

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Chapter 1

Introduction

In May 2000, water quality sampling at groundwater sources in Hertfordshire, UK, was undertaken by Three Valleys Water Ltd (renamed in 2009 as Veolia Water Three Valleys Ltd (VWTV)) in advance of changes to the Water Supply (Water Quality) Regulations (2000). The solute bromate (BrO_3^-) was to be incorporated as a new monitoring parameter with a standard of 10μg/l that would be enacted under law in 2003. Analysis revealed bromate concentrations in excess of 130μg/l at Hatfield, Bishops Rise Pumping Station (Hatfield PWS). The Environment Agency (EA) and Drinking Water Inspectorate (DWI) were immediately informed, and the abstraction well was removed from public supply.

The source of the contamination was identified as a former chemical works at Sandridge (NGR TL171104) approximately 6km west of Hatfield PWS. Following closure of the works in the early 1980s the site was redeveloped into a residential housing estate known as St Leonard's Court (SLC). Subsequent groundwater and surface water monitoring has indicated that the bromate contamination is extremely widespread (Figure 1.1) extending up to 20km east from the contaminant source and affecting an area of $\geq$ 40km^2.

The occurrence of bromate in the Hertfordshire Chalk aquifer presents a current and future threat to groundwater resources. Concentrations normally, or periodically, in excess of the drinking water standard affect 12 public supply groundwater wells operated by VWTV and Thames Water Utilities Ltd (TWUL). The total licensed abstraction for public supply in the affected area of aquifer is over 200Ml/day (White, 2007) and forms a proportion of the supply for central Hertfordshire and North London. Surface waters of the Rivers Lee, tributaries of the Colne and private abstractions are also affected.

The Chalk is a white, highly pure, biogenic limestone typically formed from $\geq$ 90% Calcium Carbonate with a minor constituent of non-carbonate components. The rock is normally considered to be a dual porosity aquifer (e.g. Foster and Milton, 1974; Black and Kipp, 1983; Barker, 1993) being comprised of a primary matrix porosity resulting from deposition and diagenesis, and a secondary fracture porosity

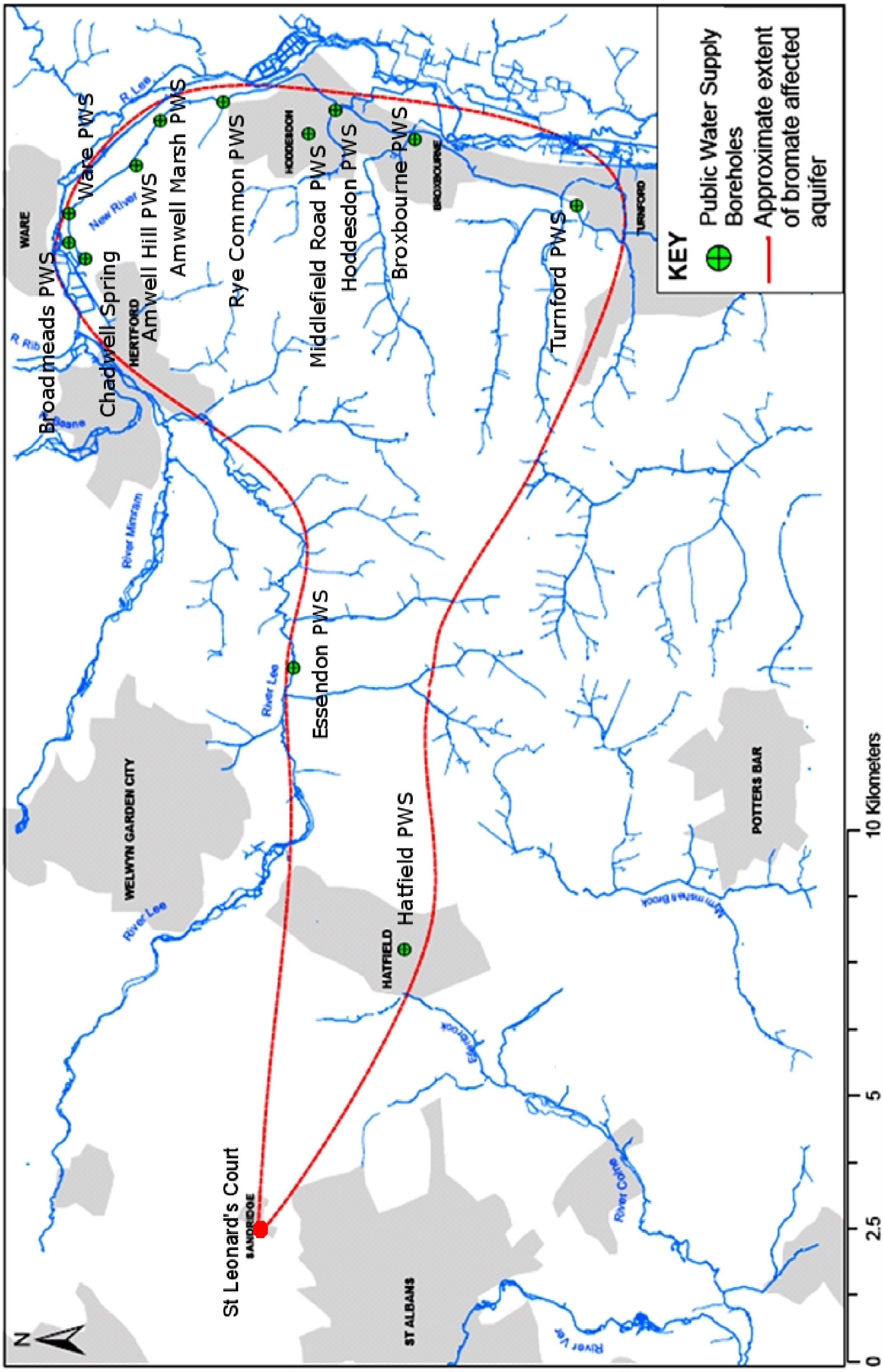


Figure 1.1: Location plan showing the extent of the Hertfordshire chalk aquifer affected by bromate contamination and the distribution of major public supply wells

arising from tectonic stress. The Chalk matrix is composed of fine grained calcium carbonate shell debris, dominantly cococclith fragments, and this granular character imparts a large primary porosity (typically $20-40\%$) which accounts for $\approx 95\%$ of the total porosity and storage. However, the small grain size means that pore spaces have extremely narrow throat sizes (typically $\leq 1\mu$m). This severely restricts the permeability of the matrix to between 10^{-3} and 10^{-1}m/day (Price et al., 1976) and on most time scales the matrix porewater is considered to be effectively immobile.

Fractures and joints (including faults) in the chalk matrix formed due to tectonic disturbances or resulting from stress release upon uplift and sub aerial exposure. The fractures typically occur in three orthogonal joint sets of small aperture ($\leq$ 5mm with the majority being $\leq$ 1mm) (Bloomfield, 1996) and account for only a very small fraction of the total porosity of the rock (typically $\leq 0.01\%$) (Price et al., 1993). As a result of their low porosity, fractures possess low storage capacity compared to the chalk matrix but where fractures are open, they are extremely transmissive and account for nearly all of the effective measured permeability of the aquifer (typically between 10^{-1}m/day and 10^{2}m/day) (Price et al., 1993).

The character of the chalk aquifer makes it a highly valuable water resource but also means that it is particularly vulnerable to pollution. Fractures dominate flow and transport and are the principal pore space through which any dissolved contaminant phase will migrate. Solutes can be exchanged between the fractures and the chalk matrix blocks by either by high head differences or by chemical diffusion which is extremely slow, typically on the order of a few centimetres per year (Barker, 1993). Figure 1.2 provides a schematic illustration of the process of dual porosity diffusion.

Owing to dual porosity processes, contamination events in chalk are highly persistent. Temporary storage in the matrix acts to retard the transport of dissolved species through the chalk and the slow rate of diffusion means that contamination can persist in the aquifer mass for long periods of time (10s - 100s of years). Dual porosity matrix-fracture diffusive exchange also attenuates the peak of a solute pulse when compared with transport that is dominated by advection and mechanical dispersion, as illustrated in Figure 1.3.

Thus with a diffusive, highly dispersive aquifer and a poorly quantified source of bromate, characterising the transport of bromate in the chalk of aquifer Hertfordshire presents a significant challenge.

1.1 Karst development in Chalk

The chalk, as with other limestones, is prone to dissolution of its principal mineral calcite ($CaCO_3$) by infiltrating water. Dissolution of the rock can enhance the porosity and hydraulic conductivity of the aquifer, particularly by increasing aper-

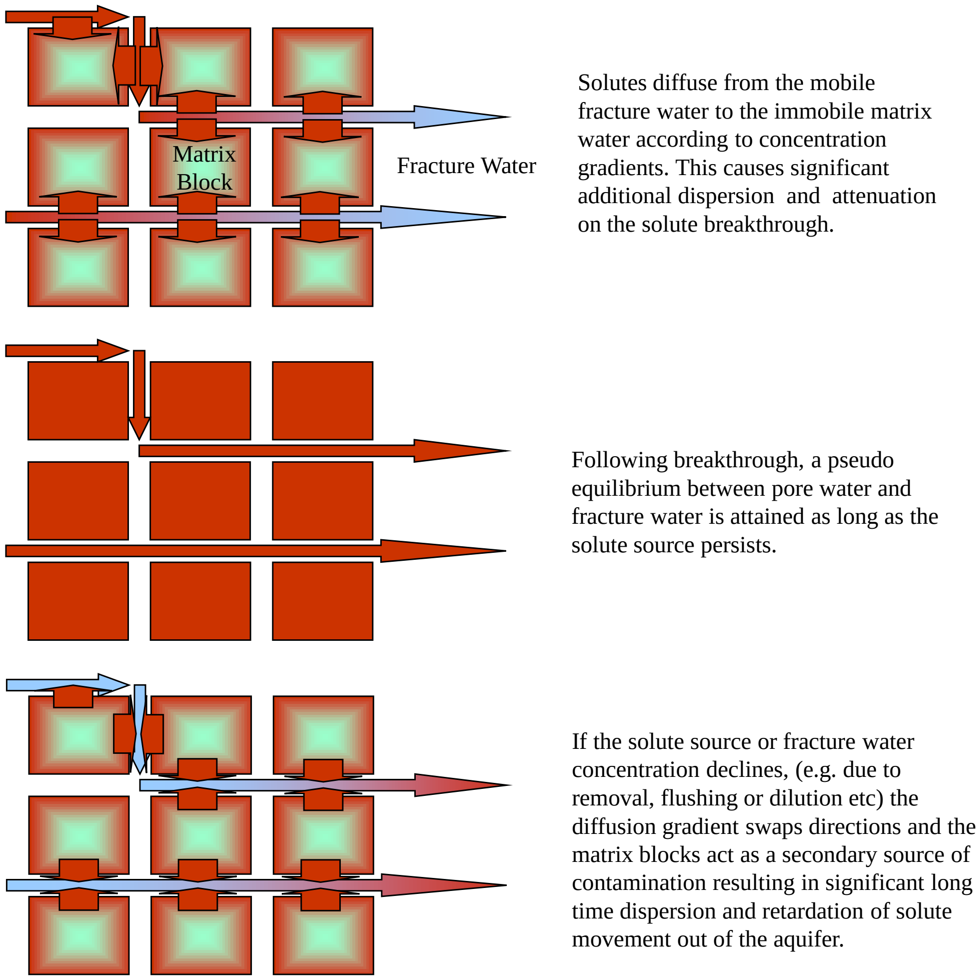


Figure 1.2: Schematic illustration of solute transport in the chalk aquifer which is formed from transmissive fractures and matrix blocks containing essentially immobile water

ture of the fractures, creating channeling in fissures or generating new dissolution void spaces such as caves and conduits.

Void development and dissolution of the chalk in the sub-surface can, but not always be inferred from the presence of surface geomorphological features such as dolines, collapse sink holes, sinking streams, swallow holes, dry valleys, springs and caves. This suite of geomorphological and hydrogeological characteristics takes its name from the type location in Slovenia and Italy called the Kras (or Karst) region (Ford and Williams, 2007) and since the 19th century the term "karst" has been used more generally to describe landscapes and subsurface features which have been dominantly shaped by processes related to dissolution of the bedrock.

The presence of an enhanced karstic porosity in the chalk aquifer has long been recognised (e.g. Docherty, 1971; Atkinson and Ingle Smith, 1974; Price, 1987; Banks et al., 1995; MacDonald et al., 1998; Maurice et al., 2006) particularly where its surface expression in the form of dolines, collapse sink holes and swallow holes occurs. In the bromate-affected chalk aquifer of Hertfordshire, development of a

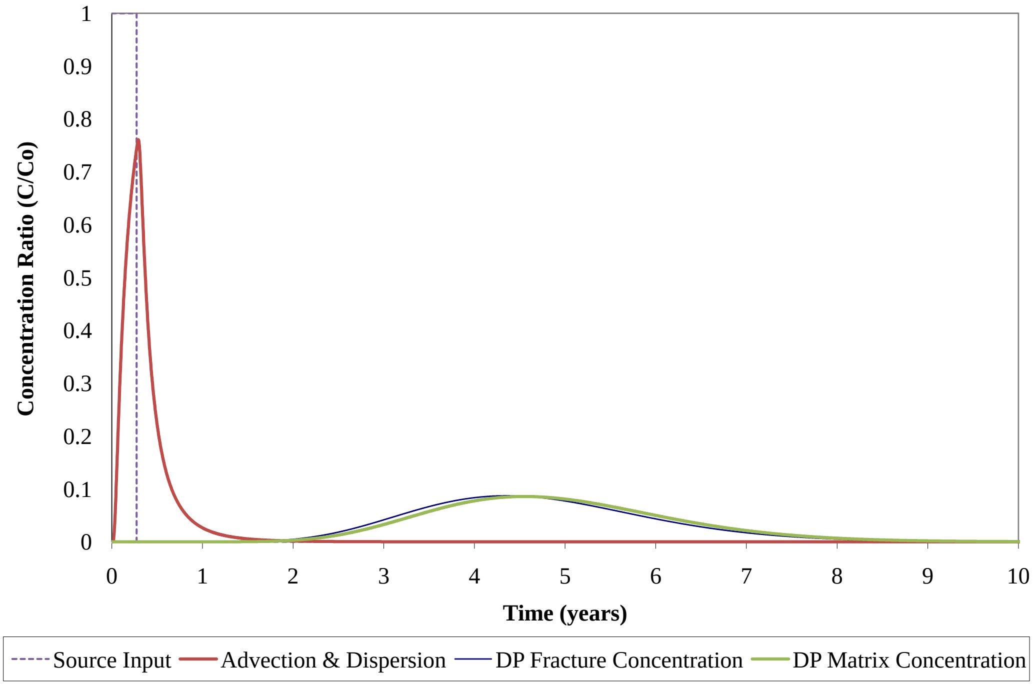


Figure 1.3: The influence of double porosity diffusive exchange between fractures and matrix (blue) delays and attenuates the solute peak compared to that of advective and mechanical dispersion only (red) for a pulse of solute transport using the analytical model of Barker (2005)

karstic enhanced fracture porosity and conduit system complicates the dual porosity flow and transport and appears to be responsible for the widespread distribution of the bromate contamination. Previous attempts to replicate and predict bromate transport in the Hertfordshire Chalk aquifer (e.g. Buckle, 2003; Assem, 2005) have been hindered by an insufficient understanding and representation of the karst flow system and by inadequately reconciling it with the dual porosity character of the aquifer.

This thesis provides a new quantitative conceptual understanding of the karst in the Hertfordshire Chalk Aquifer. This understanding has been incorporated into regional numerical groundwater flow models using a variety of possible representations in order to derive improved predictions of bromate concentrations at important receptors.

1.2 Aims

The main objective of this research is to quantitatively characterise the catchment scale karstic groundwater flow system that exists in Hertfordshire in the context of the bromate contamination through literature, field and modelling investigations. This will enable predictions to be made that are consistent with the observed aquifer features and behaviour.

Specific objectives of the research are:

- Re-evaluate previous work on the aquifer and the bromate problem in the context of the karst flow system
- Investigate the karstic system through a catchment-scale tracer test and a re-analysis of historical tracer test data
- Derive a new and improved conceptual understanding of the hydrogeological function of the Hertfordshire karst and consider the findings in terms of field observations
- Appropriately incorporate the conceptual understanding of the Hertfordshire karst system into catchment-scale groundwater flow and transport models that can be calibrated and validated against available data.
- Provide predictions of the future evolution of bromate at points of interest in the aquifer and under different future scenarios/stress conditions

1.3 Approach

The bromate contamination in the Hertfordshire chalk aquifer is of similar extent and magnitude to a plume of chloride originating from former mine workings at Tilmanstone in Kent (Headworth et al., 1980; Watson, 2004). Solute transport in the Tilmanstone plume is dominated by dual porosity diffusive exchange and Watson (2004) developed an investigatory methodology for characterising these transport processes in the Chalk aquifer in order to derive predictions of chloride transport.

Given the apparent similarity in scale between the Tilmanstone plume and the Hertfordshire bromate contamination it was initially considered that the "Tilmanstone Methodology" could be applied and tested in the Hertfordshire Chalk Aquifer. However, following a review of previous work undertaken on the bromate problem and in particular, data relating to the presence of karstic flows in Hertfordshire, which were not observed at Tilmanstone. It became apparent that both karstic and dual porosity flow and transport processes were influencing bromate transport. As a result, the Tilmanstone Methodology would not be able to fully characterise this flow system. In particular, the degree to which the karst system influences flow and transport in Hertfordshire was poorly quantified.

To address these issues, a catchment scale groundwater tracer test was designed and undertaken in order to investigate features and behaviour of the karst flow system, determine appropriate hydrodynamic parameters and attempt to delineate the extent of karstification. Based upon the interpretation of new data obtained by the tracer tests, as well as the re-evaluation and interpretation of existing data, a new conceptual model of the aquifer function of Hertfordshire Chalk karst has been developed and where possible, quantitative parameters determined from observations are applied.

The new conceptual model is used as a framework for developing new regional groundwater flow and transport models incorporating a representation of the karst flow system and which can take advantage of parameters and new data obtained from the tracing to calibrate against observations. However, since the computational and mathematical models available are not necessarily consistent/adequate representations of a discrete, rapid, heterogeneous and anisotropic karstic flow system, a number of models have been developed to incorporate different possible representations of the karst. These model representations provide experimental platforms from which to obtain predictions of future evolution of contaminant concentrations at target locations. The uncertainty associated with these predictions is also considered.

1.4 Thesis Structure

An outline of the structure of this thesis is provided below:

Chapter 2 describes the known history of the Bromate contamination in Hertfordshire in terms of its detection, observed distribution, trends and behaviour of bromate in the aquifer. It also establishes a business case for the present research which considers the financial and operational impacts of the bromate contamination.

Chapter 3 describes the geological setting of the Hertfordshire Chalk aquifer and its properties. This includes a description of the chalk aquifer, its stratigraphy, and its relationship with overlying and adjacent units. The hydrogeology of the aquifer is described, including, observed piezometry and temporal variations in water levels. Based upon this review a conceptual hydrostratigraphy of the Hertfordshire Chalk aquifer is developed.

Chapter 4 describes the distribution of karst landforms and aquifer characteristics in Hertfordshire. It summarises previous work on the Hertfordshire karst and the conceptual understanding that had been established. It also includes new additional field surveys and reinterpretation of previous tracer testing to outline a preliminary conceptual model of the karst.

Chapter 5 describes the requirement for a new suite of tracer tests and the strategy by which these new tests were designed. A critical assessment of the results of tracing is presented.

Chapter 6 provides a re-interpretation of the function of the Hertfordshire Chalk karst. Chapter 6 also describes the features of the karst system which influence the transport of bromate and therefore must be adequately represented in groundwater flow and transport models.

Chapter 7 contains a review of previous model development with respect to the bromate contamination. It also describes how a new groundwater model was developed to include karst representation of the aquifer. Chapter 7 also describes the calibration and validation of these models against observations, including the tracer test data and comments critically on their inherent assumptions, validity and limitations.

Chapter 8 uses the model described in Chapter 7 to derive likely ranges of future bromate concentrations at target receptors. Each prediction is based upon a likely or possible future aquifer state or remediation scenarios. The assumptions, limitations and uncertainty associated with each predictive scenario are discussed.

Finally, Chapter 9 discusses and summarises the findings of this work in the context of the objectives outlined in Section 1.2. It also discusses the wider implications of this work when considering solute transport elsewhere in the Chalk aquifer.

Chapter 2

The Bromate Problem and the Business Context

This chapter describes the characteristics of bromate as a groundwater contaminant and the body of legislation relating to groundwater and groundwater contamination in the United Kingdom. The impact of the bromate contamination and the constraints of legislation are used to establish a business context for Veolia Water Three Valleys Ltd and Thames Water Utilities Ltd. In 2009, Three Valleys Water Ltd were renamed as Veolia Water Three Valleys, and are hereafter referred to as such/

2.1 Bromate as a Groundwater Contaminant

Bromine, occurring dominantly as the anion bromide (Br^-) is a naturally occurring trace element in groundwater originating from the dissolution and weathering of minerals present in the aquifer material in additional to a tracer component of rainfall recharge. In the unconfined chalk of Hertfordshire, bromide has been determined to have a baseline (i.e. natural) concentration of between 40μg/l and 400μg/l with a median of 50μg/l (Shand et al., 2004). In the confined parts of the aquifer, bromide concentrations are greater ranging between 50μg/l and 500μg/l with a median of 130μg/l (Shand et al., 2004).

Bromate ($BrO_3{}^-$) is an inorganic species of bromine and oxygen, occurring either as the dissolved anion $BrO_3{}^-$ or forming salts, the most common of which are sodium bromate ($NaBrO_3$) and potassium bromate ($KBrO_3$). Bromate is not known to occur naturally in groundwater. The most commonly reported source of bromate in water is as a disinfection by-product of bromide loaded water (WHO, 2005), which can also occur naturally under rare circumstances e.g. due to a photolytic reaction caused by intense sunlight (Ramallo, 2007).

Bromate salts are produced commercially. Potassium bromate is used as a flour enhancer and in the malting of barley (USFDA, 2009) and other salts are used in the manufacture of permanent wave ("perm") hair products and photographic chemicals. Because the most common origin of bromate in water is as a by-product of treatment processes the occurrence of bromate in untreated groundwater in Hertfordshire was unusual and immediately led to suspicion of anthropogenic contamination.

Ingestion of bromate in drinking water can cause acute symptoms including nausea, vomiting, abdominal pain, anuria and diarrhoea and can also affect the central nervous system (USEPA, 2001). Doses in excess of 185mg BrO_3^- per kg body weight can lead to renal failure and deafness with a lethal dose estimated to be between 200 – 500mg BrO_3^- per kg body weight (WHO, 2005). Bromate contamination also leads to ecological damage, affecting waterborne organisms both through acute toxicity and long term pathological damage (Butler, Godley, Lytton and Cartmell, 2005)

In-vivo studies of rats have indicated long term exposure to bromate can cause mutagenic changes and an increased frequency of cancer incidence and as a result, Bromate is considered to be a probable human carcinogen linked to thyroid and renal cancer (WHO, 2005). Presently, no data exist to suggest other non-carcinogenic risks following long term exposure to bromate (USEPA, 2001). The World Health Organisation (WHO) have determined that a technically achievable drinking water standard of 10μg/l would be associated with an upper bound excess lifetime cancer risk of 5×10^{-5} (WHO, 2005). A limit of 10μg/l was incorporated into the United Kingdom Water Supply (Water Quality) Regulations 2000.

An epidemiological study by Aylin et al. (2003) on the incidence of renal and thyroid cancers in areas of Hertfordshire which may have been affected by bromate prior to identification of the contamination could not identify a statistically significant increase in cancer incidence.

2.1.1 Transport of Bromate

Little information exists regarding the behaviour of bromate in the groundwater environment. Butler, Godley, Lytton and Cartmell (2005) report that bromate is highly stable in solution with low chemical reduction rates and is generally conservative. Bromate possess similar chemistry and solubility to nitrate (NO_3^-) and perchlorate (ClO_4^-), which also appear to be conservative under most groundwater conditions, although like bromate, both can be reduced by microbial action under anoxic conditions.

Comparison can also be made with the transport of the bromide ion which is typically non-reactive and conservative under most groundwater conditions, and does not readily form complexes, participate in redox reactions, or sorb onto mineral or organic material. Bromide has favourable properties as a groundwater tracer and has been successfully used as such in the chalk aquifer (e.g. Besien et al., 2000;

Gooddy et al., 2002). The natural occurrence of bromide in groundwater, particularly in combination with chloride (Cl^-) has been used to infer seawater mixing over geological time and Cl^-/Br^- relationships have been used to investigate the hydro-chemical evolution of aquifers (e.g. Davis et al., 2001).

In addition to bromate contamination, the chalk aquifer of Hertfordshire has also been affected by bromide contamination. However since bromate forms the principal contaminant of concern with regard to health affects and regulatory standards, this research focuses entirely upon the transport of the bromate contaminant. Fitzpatrick (2010) discusses the distribution, transport and possible relationship between bromate and bromide in detail.

This research does not directly address the transport properties of the bromate solute beyond that which is explicitly due to the characteristics of the chalk aquifer in Hertfordshire. Some broad assumptions are therefore made based upon what are considered to be the likely transport properties of bromate:

- Bromate is considered to be a conservative, non-sorbing solute
- Since the Hertfordshire Chalk Aquifer is largely unconfined, the reduction of bromate to bromide is considered to be negligible

2.2 Observed Distribution and Behaviour of Bromate in the Hertfordshire Chalk Aquifer

This section provides an overview of the observed distribution of bromate and where applicable, apparent temporal trends and relationships that are observed. A more detailed description of the spatial distribution and magnitude of bromate concentrations is provided elsewhere (e.g. Buckle, 2005; Hay and Buckle, 2006; Fitzpatrick, 2010).

2.2.1 Spatial Distribution

The distribution of locations with detectable concentrations of Bromate (MDL $\approx 1\mu$g/l (Butler, Lytton, Godley, Tothill and Cartmell, 2005)) in groundwater and surface water are shown in Figure 2.1. The affected locations extend in a fan like pattern from Sandridge, increasing in width and decreasing in concentration eastward, being over 1000μg/l at monitoring locations near to the contaminant source between $100 - 500\mu$g/l in the vicinity of Hatfield PWS and between $1 - 50\mu$g/l at the Lee Valley.

The contamination extends in a south easterly direction from the source location sub-parallel to the Sandridge dry valley. The main direction of contamination reflects that of the regional groundwater flow but an easterly dog-leg occurs at the

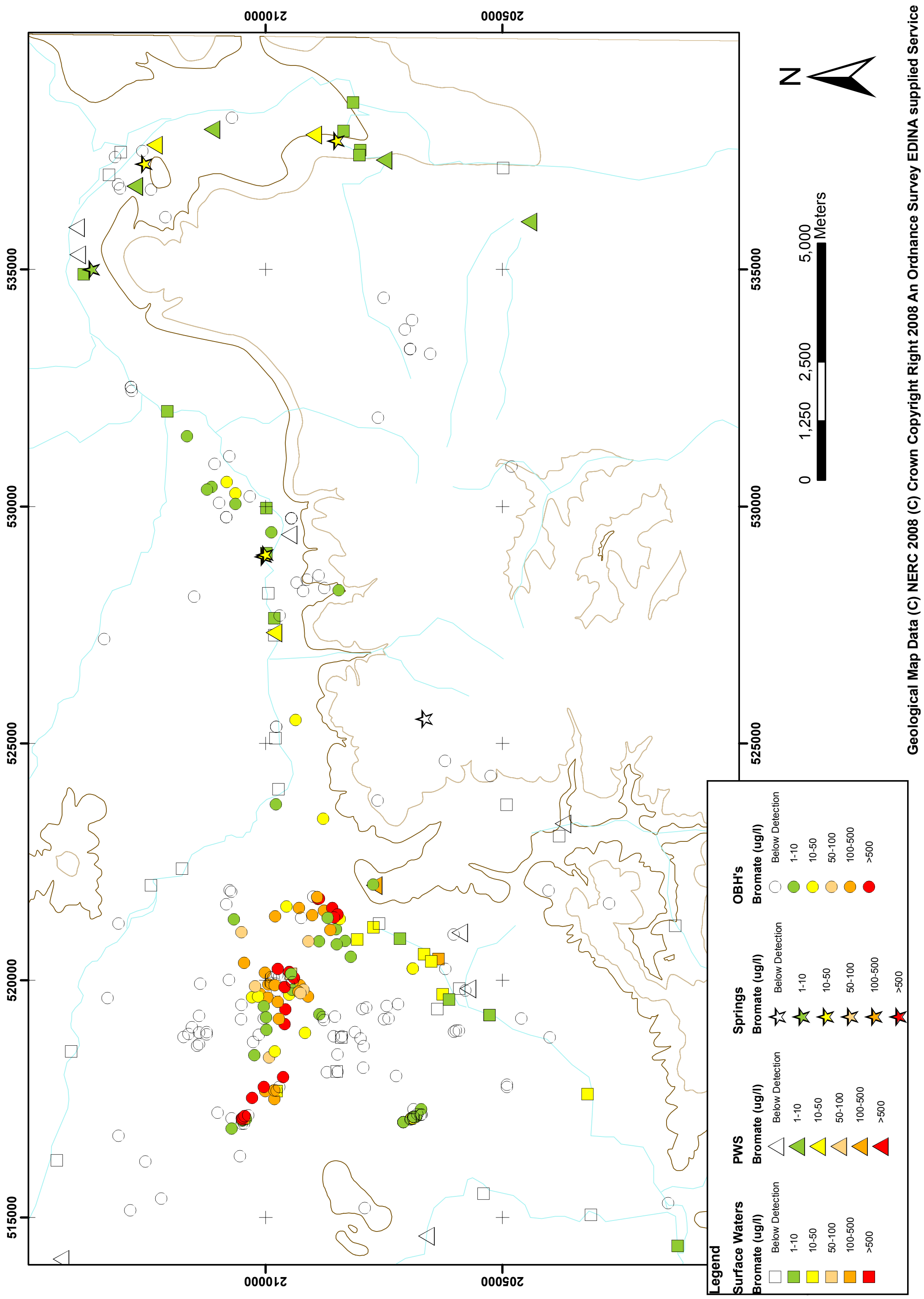


Figure 2.1: Spatial distribution of median bromate concentrations measured in groundwater and surface water in the period 2000-2006

approximate boundary with the Vale of St Albans and is also associated with an apparent increase in width of the affected locations from less than 0.5km in the Chiltern dip slope to approximately 1km. The total width of the affected region reaches approximately 1.5km in the centre of the Vale of St Albans.

In the vicinity of Hatfield the bromate occurs within a relatively narrow zone between 1.5km and 2km in width between the northern edge of the town and Hatfield PWS and is also consistently observed at the Park Street Observation Borehole on the eastern boundary of the town and at Mill Green to the north.

Between Hatfield and the Lee Valley, the availability of monitoring locations is limited and the apparent bromate 'plume' is less well defined. The occurrence of bromate also appears to be intermittent and at low concentration. Only two locations between Hatfield and the Lee Valley have shown consistently high concentrations of bromate, the VWTV abstraction source at Essendon PWS and a groundwater spring at Arkley Hole. The magnitude of concentrations and temporal variations of bromate concentration at both these locations appears to be similar. Bromate has also been detected to the northeast beyond Arkley Hole Spring, however these monitoring locations are located within and adjacent to a landfill and it cannot be ruled out that there may be an alternative source of bromate within the landfill material. Between Arkley Hole Spring and the Lee Valley, there few monitoring points available within the likely main pathways of bromate migration and the Veolia Water Three Valleys abstraction well at Water Hall PWS has remained unaffected by bromate contamination.

Within the Lee Valley itself, between Hertford and Cheshunt, a distance of approximately 10km, bromate has been detected at all of Thames Water Utilities Limited's Northern New River (NNR) groundwater abstraction sources south of Amwell Hill. Springs at Chadwell, Emma's Well and Lynchmill are also affected. Bromate has not been detected at any other monitoring location in the vicinity of the Lee Valley and appears to only occur at potentially harmful concentrations at public water supply wells and springs (Hay and Buckle, 2006).

The spatial distribution of the bromate contamination has been stable since monitoring begun in 2000 (Hay and Buckle, 2006). On the apparent margins of the affected area of aquifer where bromate concentrations are close to detection limits there are only sporadic occurrences of bromate above this limit and the drinking water standard is rarely exceeded. There is little evidence to suggest migration of bromate beyond the presently observed distribution. However due to the sparse monitoring network, particularly in the south and east of the region, this cannot be ruled out.

2.2.2 Temporal Variations

2.2.2.1 Variations Close to the Contaminant Source

Figure 2.2 shows the temporal variation of bromate concentrations between 2000 and 2009 for the area between Sandridge and Hatfield Quarry, a gravel extraction quarry located approximately in the centre of the Vale of St Albans.

At Orchard Garage there appears to have been an initial decline between 2000 and 2001 from approximately 4000μg/l to approximately 1000μg/l which then rebounded in 2002 to approximately 1500μg/l. This could possibly be attributed to relatively high rainfall in 2001 which led to localised groundwater flooding in the Sandridge dry valley and may have diluted bromate concentrations. Concentrations remained in the range 1500μg/l to 2000μg/l until 2006, thereafter there appears to have been a slight decline in to $500 - 1000\mu$g/l from 2007.

At Nashes Farm there appears to have been a decline in bromate concentration from approximately $2500-4000\mu$g/l in 2000 to around 1000μg/l in 2002. Thereafter, bromate concentrations have been generally stable in the range from $900-1400\mu$g/l.

At Hatfield Quarry, there are a number of monitoring locations; time series are presented (Figure 2.2) for borehole WM12, in the apparent centre of the affected area and are representative of other monitoring locations in this area (Hay and Buckle, 2006). In general, a rising trend is observed from approximately 700μg/l in 2000-2001 to over 1000μg/l by 2007. Little apparent seasonal variation is observed although there is some variability in measurements.

2.2.2.2 Variations in the Vicinity of Hatfield

Figure 2.3 shows time series of bromate concentrations for Hatfield Business Park on the approximate western boundary of Hatfield and at Hatfield PWS.

At Hatfield Business Park concentrations of bromate are normally in the range of $400 - 600\mu g/l$ with a rising trend apparent between 2000 and 2003. Unusually low concentrations on the order of 450μg/l were recorded in April and May 2001, but the cause of this variation is unknown. There are no data in the period between August and December 2002, however, when sampling resumed concentrations were in a similar range, although showing slightly greater variability between 300μg/l and 750μg/l and a possible slight increase in concentrations over the same period.

At Hatfield PWS concentrations rose following initial detection of the bromate at concentrations of 150μg/l in May 2000 to over 300μg/l in November 2000. This period was associated with continuous pumping of groundwater to waste. Thereafter, abstraction ceased and a decline in concentrations occurred to $100 - 150\mu$g/l in May 2001. Subsequently there was an annual rise in concentrations reaching a peak in July 2005 of over 400μg/l.

In July 2005 scavenge pumping began at Hatfield PWS and has since been pro-

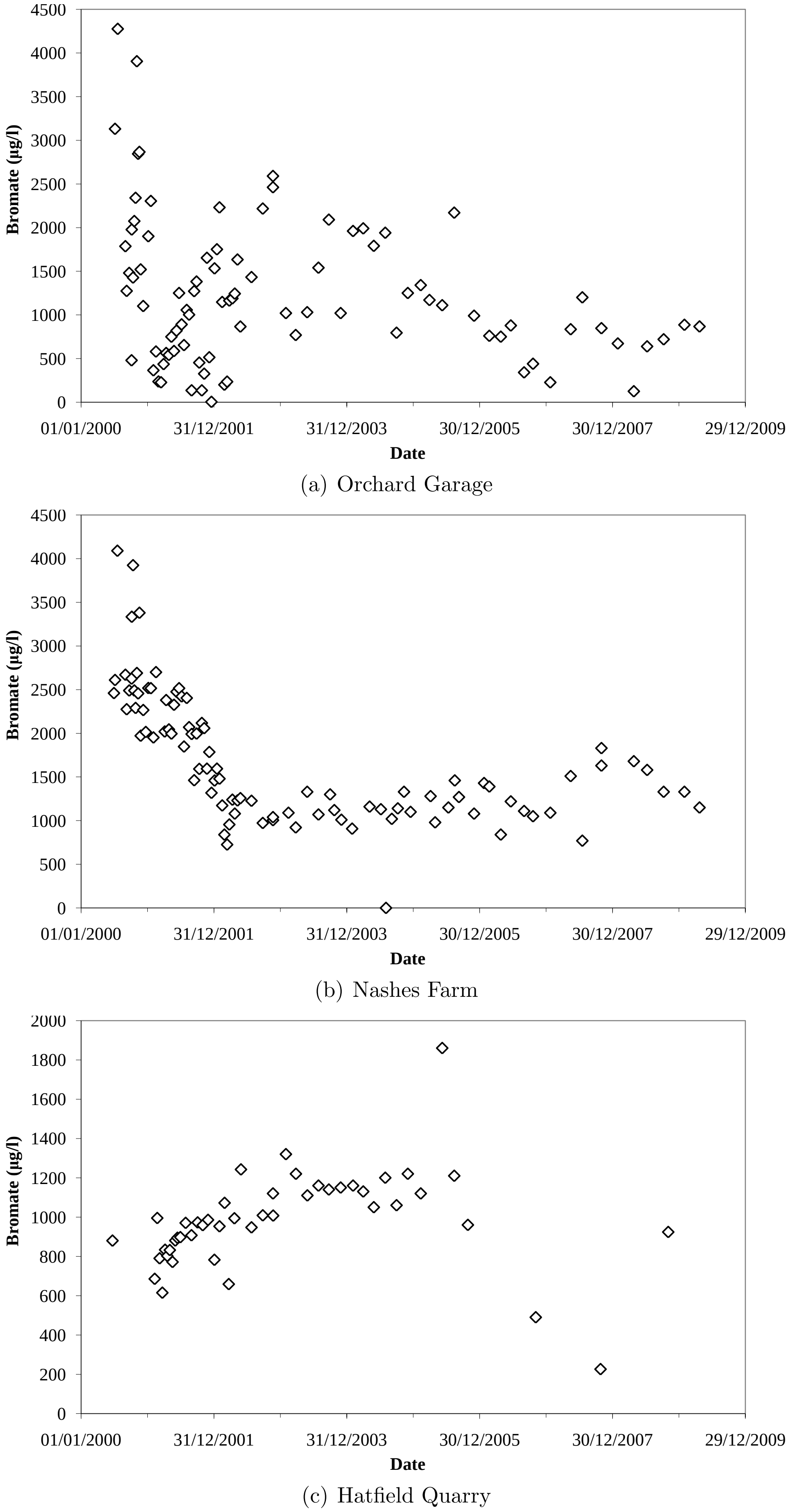


Figure 2.2: Temporal variations in bromate concentrations close to the contaminant source (Orchard Garage) on the margins of the Vale of St Albans (Nashes Farm) and in the centre of the Vale of St Albans (Hatfield Quarry). Data were obtained and used with permission from the Environment Agency

moted as an interim remediation method in order to protect downgradient sources. Since July 2005 there has been a reduction of bromate concentrations to the range $200 - 300\mu g/l$ although sporadic values $\geq 400\mu g/l$ and $\leq 200\mu g/l$ occur. Under pumping conditions, bromate concentrations measured at Hatfield PWS are positively correlated with abstraction rate, i.e. greater abstraction lowers the measured concentration of bromate. This is thought to reflect increased dilution from bromate-free water (Bishop and Sage, 2006; Fitzpatrick, 2007) and is responsible for the general decline in concentrations at Hatfield PWS since 2005.

The effectiveness of the scavenge pumping at Hatfield PWS and other locations is discussed in Section 2.5.1.1 and in greater detail by Bishop and Sage (2006) and Fitzpatrick (2007).

2.2.2.3 Variations East of Hatfield

Relatively few monitoring locations are available where bromate has been consistently detected in the area between Hatfield and the Lee Valley, only Essendon PWS and Arkley Hole Spring have time series (Figure 2.4).

At Essendon PWS bromate concentrations were observed in summer of 2000 to be between $10 - 20\mu g/l$. This fell to $\leq 10\mu g/l$ in the winter of 2000/2001, followed by a rise in concentrations in the summer of 2001 to between $15 - 30\mu g/l$. The seasonal trend of relatively high summer concentrations and low winter concentrations continues to the present day and is superimposed upon an annual year on year increase in bromate concentration reaching a peak of over $50\mu g/l$ in summer 2005. Subsequently the Hatfield scavenge pumping has resulted in a reduction of bromate concentrations to between $30 - 40\mu g/l$ although the seasonal fluctuation still occurs. Lytton (2005) has correlated this seasonal pattern to variation in soil moisture deficit.

Data from Arkley Hole spring are lower in frequency but show similar overall pattern to those at Essendon PWS with a generally increasing trend between 2002 and 2005. After July 2005, there appears to be a reduction in bromate concentration probably associated with the scavenge pumping at Hatfield PWS.

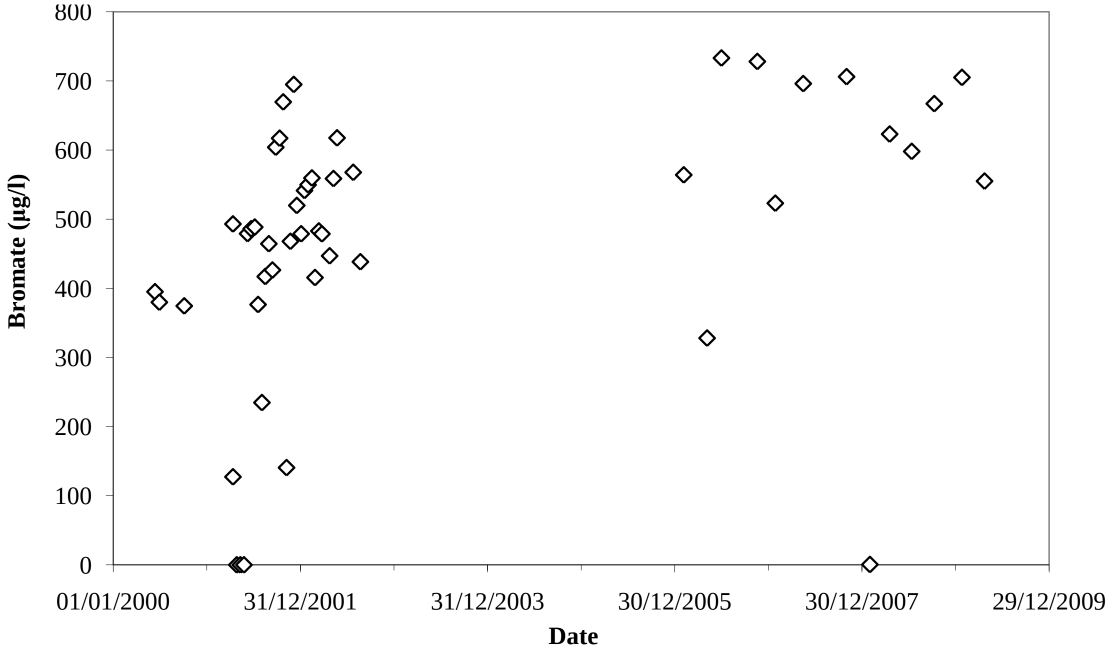
2.2.2.4 Variations in the Northern New River (Lee Valley) Wells

Thames Water Utilities Ltd's Northern New River wells are grouped by their geographic location and impact from bromate contamination. The central (Hoddesdon PWS, Middlefield Road PWS) and southern wells (Broxbourne PWS, Turnford PWS) typically show higher concentrations than the northern wells (Amwell Hill PWS, Amwell Marsh PWS, Rye Common PWS) and at the northernmost wells (Amwell End PWS, Ware PWS and Broadmeads PWS) bromate is rarely observed above the detection limit. All locations where bromate is consistently observed show a rise in concentration between 2001 and 2005 (Figure 2.5), however, the 2004-2005 concentrations were generally lower than those recorded in 2003.

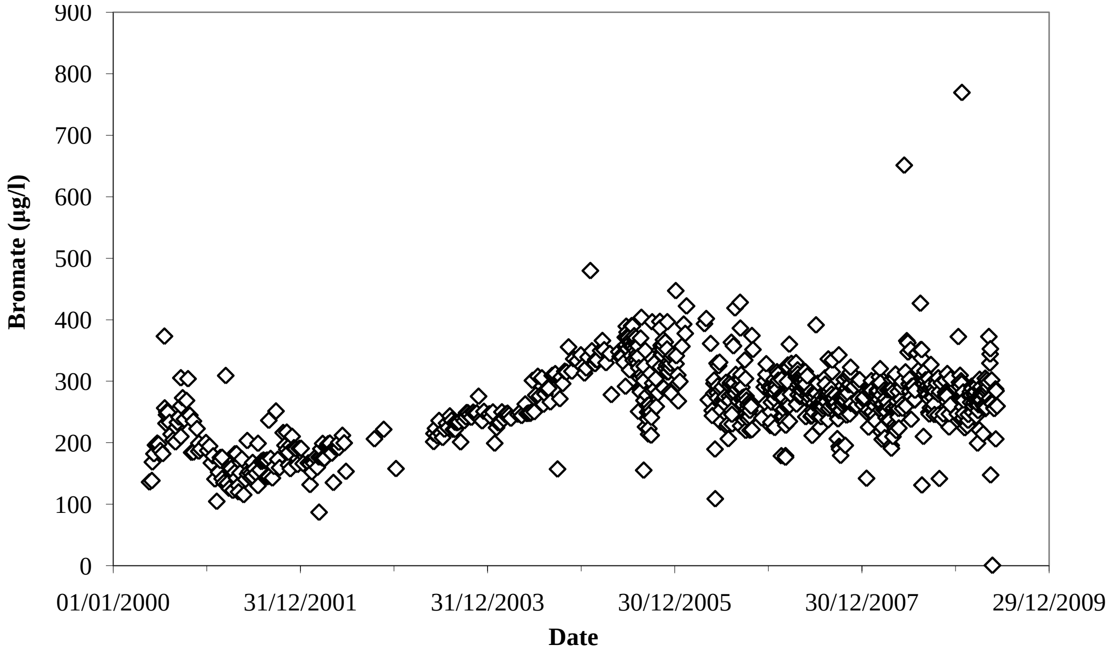
Amwell Hill, Amwell Marsh and Rye Common PWS show bromate concentrations between 0.6μg/l and 33.6μg/l. Amwell Marsh shows the highest concentrations in this group, however Rye Common PWS shows greater variability with the highest peak concentration recorded. Peak concentrations usually occur in the spring between March and May and are most often observed in April.

The central NNR wells (Middlefield Road PWS, Hoddesdon PWS) show bromate concentrations between 0.6μg/l and 67.2μg/l with the majority of observations in the range 7μg/l to 50μg/l. There is close agreement between concentrations measured at both locations but Hoddesdon PWS typically shows higher and more variable concentrations than Middlefield Road PWS. The timing of peak concentration occurs slightly later than the northern wells between May and June.

The southern NNR wells (Broxbourne PWS, Turnford PWS) show bromate concentrations in the range from 0.6μg/l to 55.9μg/l with Broxbourne typically being more variable and showing slightly higher concentrations than Turnford PWS. The timing of the summer peak concentration is again later than further north, usually between June and September.

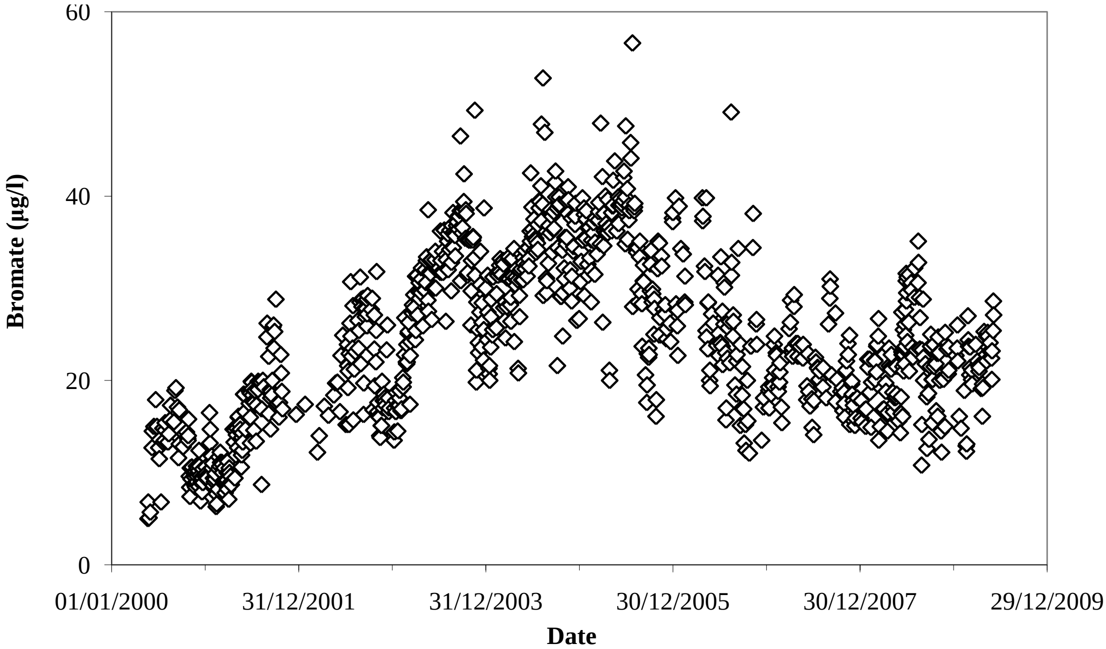


(a) Hatfield Business Park

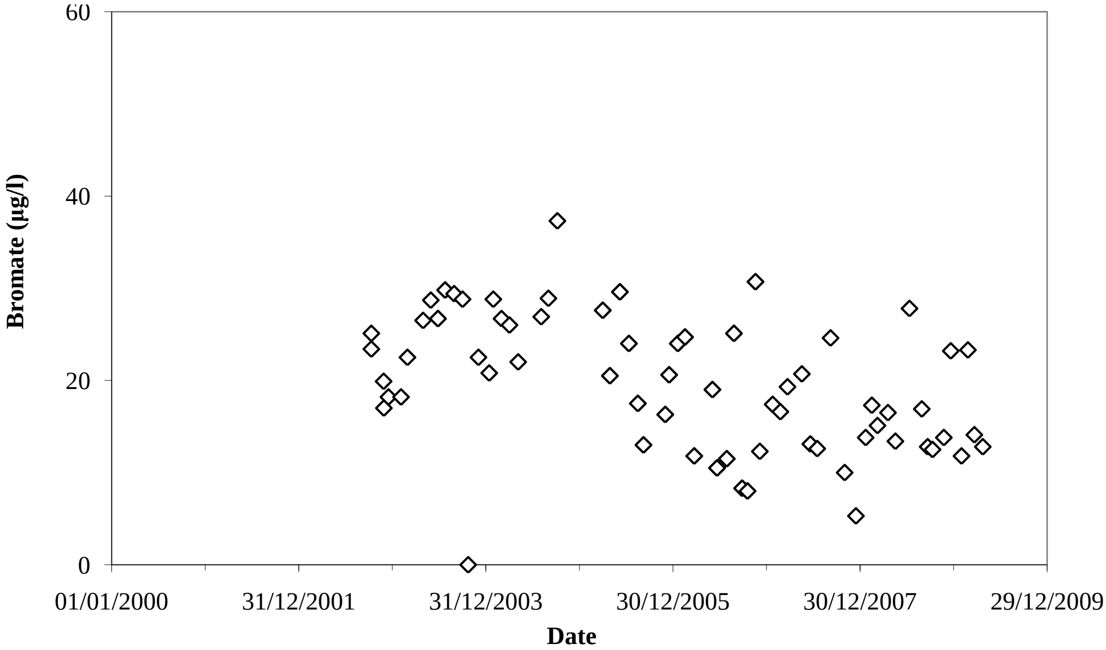


(b) Hatfield PWS

Figure 2.3: Temporal variations in bromate concentrations in the area of Hatfield. Data were obtained and used with permission from Veolia Water Three Valleys Limited and The Environment Agency

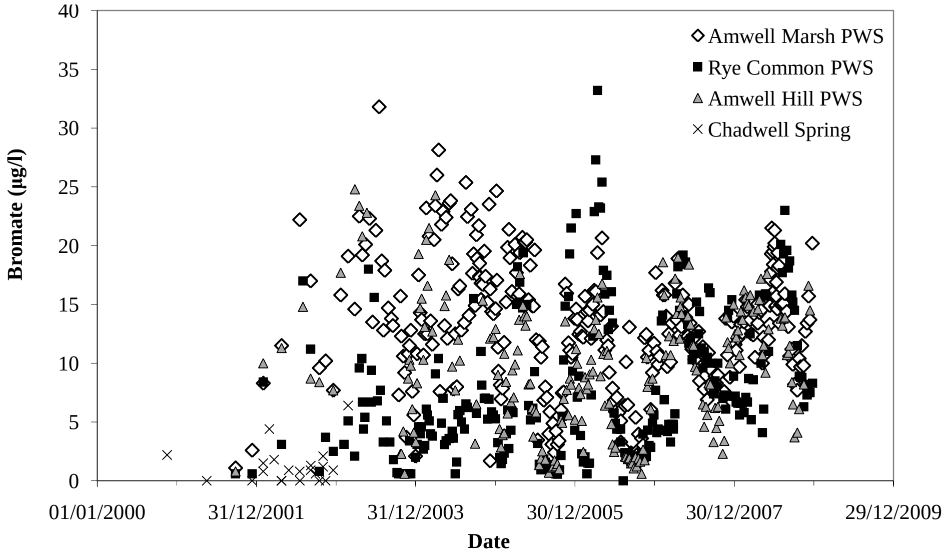


(a) Essendon PWS

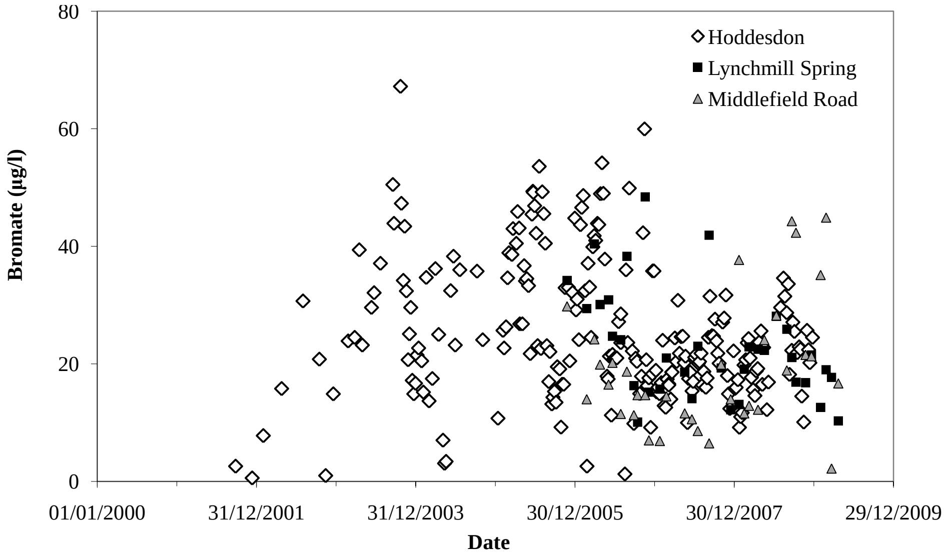


(b) Arkley Hole Spring

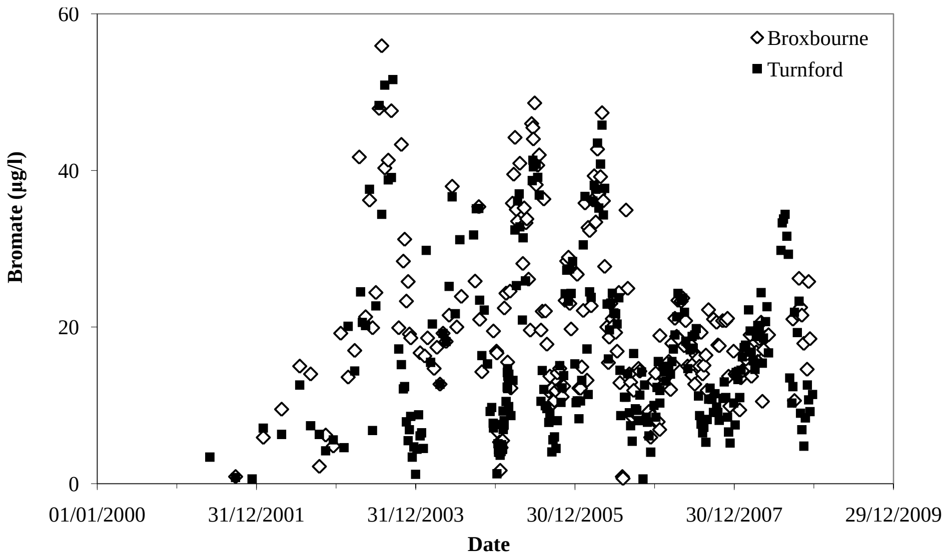
Figure 2.4: Temporal variations in bromate concentrations in the area east of Hatfield. Data were obtained and used with permission from the Veolia Water Three Valleys Limited and The Environment Agency



(a) Northern Lee Valley Wells and Springs



(b) Central Lee Valley Wells and Springs



(c) Southern Lee Valley Wells

Figure 2.5: Temporal variations in bromate concentrations in Northern New River Well field (Lee Valley). Data were obtained and used with permission from Thames Water Utilities Ltd

2.3 Regulation of Groundwater in the UK

Groundwater and contamination of the subsurface has been subject to a long history of regulation, this section describes the current regime of legislation that exists in the UK relating to the use and protection of groundwater resources.

2.3.1 The Environmental Protection Act (1990)

The Environmental Protection Act (1990) introduced a system of integrated pollution prevention and control (PPC) under which permits were issued to ensure industries operated under controlled consents when undertaking a potentially polluting activities and in particular to prevent unlawful discharges to soil and controlled waters, including groundwater. It also includes provision for dealing with offences committed due to a breach of this regime. Part IIA of the Environmental Protection Act, and the related Contaminated Land Regulations 2000, refer to land which has become contaminated not as a result of a breach of a pollution prevention control (e.g. as a result of historical pollution). Part IIA requires local authorities to investigate, identify and give notice of sites which are contaminated land. This is defined under the Act as follows:

> *"Any land which appears to the local authority in whose area it is situated to be in such a condition, by reason of substances in, on or under the land, that (a)significant harm is being caused or there is a significant possibility of such harm being caused; or (b)pollution of controlled waters is being, or is likely to be, caused"* Part IIA, The Environmental Protection Act (1990)

Sites designated as contaminated land are registered by the appropriate Local Authority unless such site is considered a matter of national security. Enforcing authorities have a regulatory duty to require remediation of contaminated land. This is accomplished by serving a remediation notice upon an appropriate person or persons that specifies what is required in order to remediate the site. When a remediation notice is served the site becomes a special site and the Environment Agency, rather than the Local Authority, becomes the enforcing authority. An "appropriate person" is defined within the act as:

> *"Any person, or any of the persons, who caused or knowingly permitted the substances, or any of the substances, by reason of which the contaminated land in question is such land to be in, on or under that land is an appropriate person."* Part IIA, The Environmental Protection Act (1990)

Appropriate Persons are responsible for meeting the requirements outlined in the remediation notice to improve and eliminate the health risks arising from the contaminated land and if applicable other affected land. If more than one Appropriate Person is identified for a site then the a remediation notice can be served on both persons and must apportion the cost and remediation for which each is responsible. Failure to comply with a remediation notice is a criminal offence and may be subject to a prosecution and fine. If an appropriate person fails to comply, if an appropriate person cannot be determined, or if it is otherwise agreed, then remediation can be carried out by the enforcing authority, however, provision still exists in this eventuality for the enforcing authority to recover remediation costs from any appropriate person(s) should they be later identified. Appropriate persons have the right of appeal against any remediation notice served.

2.3.2 The Water Industries Act (1991)

The Water Industries Act 1991*a* sets out the legal framework for water and sewerage supply in England and Wales. It includes regulations relating to the appointment of appropriate companies to provide and operate water supplies. The act contains practical and financial regulations as to how Water Utilities are allowed to operate and supply water and sewerage. Part II, Chapter III of the act includes regulations on the maintenance of a secure supply and issues relating to water quality and wholesomeness. It establishes that water supplied must be of wholesome quality and that contaminating water resources, either knowingly or through negligence, is a criminal offence as is supplying such water for human consumption.

2.3.3 The Water Resources Act (1991)

The Water Resources Act (1991*b*) act established the Environment Agency (formally known as the National Rivers Authority) and defines the responsibilities of the agency with regard to management and protection of water resources in England and Wales. It includes the definition of controlled waters and regulations relating to water resource management, pollution, flooding, fishing and navigation. The act contains guidelines for managing abstractions of and discharges to controlled waters in order to maintain the volume and quality of water resources in the form of licensing. Part 5 of the Water Resources Act concerns the pollution of controlled waters by controlled and uncontrolled discharges and abstractions and contains articles by which notices may be served against persons deemed to be responsible for such pollution.

2.3.4 The Groundwater Regulations (1998)

The European Union Groundwater Directive (80/68/EEC) is enacted in the UK as the Groundwater Regulations (1998) and under Regulation 15 of the Waste Management Regulations. The aim of the directive is to control and prevent polluting materials from being released into the groundwater environment to ensure protection of groundwater used as a drinking or other water resource. It is enforced primarily to control waste disposal or discharges but also s enforced against deliberate or accidental releases if there is an unacceptable risk.

Controlled substances are divided into two lists; List 1 and List 2.

- Substances on List 1 should be prevented from entering groundwater directly or indirectly under all circumstances unless concentrations are low enough to not cause detriment to groundwater quality.

- List 2 Substances can only be discharged in limited concentrations and only if no deterioration of groundwater quality will result.

Bromate does not appear on either List 1 or 2 of the regulations but since it has been shown to cause mutagenic and carcinogenic symptoms (Section 2.1), the regulations make allowance for any such substance to be controlled in the same manner as a List 1 substance.

2.3.5 The Water Framework Directive

The Water Framework Directive (WFD) is a wide reaching piece of legislation with the aim of establishing a framework to protect and restore clean water and to ensure future sustainable use. The core principal is to manage water resources at a basin or catchment scale independent of administrative and international boundaries. EU member states are required to classify the status of their inland and coastal water bodies, including groundwater, within defined River Basins and to develop sustainable resource management plans for each basin which aim to maintain or improve the status.

Each surface and groundwater body defined under the directive is required to achieve “Good Status” by 2015. The precise meaning of “Good status” is specific to the water body in question and will vary depending upon the natural environment, geology as well as anthropogenic factors, however “good status” is likely to constitute low levels of anthropogenic pollution and a healthy and diverse ecosystem.

In the UK, the Water Framework Directive was adopted by law in 2003. Draft River Basin Management plans were published in December 2008, these draft plans are under consultation until June 2009. The draft plans will be finalised in December 2009 and by the end of 2009 programs of measures taken to improve river basin water quality status must begin to be implemented. The Draft River Basin

Table 2.1: Current status of water bodies as defined in Draft River Basin Management Plan for the Thames Region (Environment Agency, 2009)

	Water Body			
Parameter	Upper Lee	Lower Lee	Mymmshall Brook	Chalk Aquifer
Ecological Status	Poor	Poor	Moderate	-
Chemical Status	Failing	Failing	Poor	
Quantitative Status	-	-	-	Poor

Management Plan for the Thames region (Environment Agency, 2009) includes the Rivers Lee, Mimram and Colne and their tributaries, all of which are within or adjacent to the bromate affected area of Hertfordshire. It also includes groundwater in the Hertfordshire Chalk aquifer. Current status as defined in the River Basin Management plans is presented in Table 2.1

2.3.6 The Drinking Water (Water Quality) Regulations 2000

The Drinking Water (Water Quality) Regulations 2000 control the wholesomeness of water supplied to consumers for the purposes of drinking water. It ensures that water does not contain bacteria or substances at concentrations that would present a risk to human health when measured at the consumers tap. The regulations also set out monitoring requirements including the numbers of, standards of analysis and frequency of water sampling. The regulations also include specification of the treatment that must be applied and the materials used to construct water supply networks. Water quality must meet prescribed standards for 4 microbiological parameters and 26 chemical parameters, including bromate which was introduced as a new parameter in 2000 and must be at concentrations $\leq 10\mu$g/l.

2.3.7 Legislative Responsibility

The legislation outlined above comprises only a part of the total body that deals with groundwater, although it represents the key articles that have the greatest relevance to the bromate contamination. The legislation is complimentary and when considered as a package it serves the following overall purposes:

- To maintain the availability of water resources
- Protect those resources from pollution and over abstraction
- Ensure the quantity and quality of available water is improved in the future

The Environment Agency, is responsible for enforcing most of the legislation. However responsibility is also placed upon Water Utilities to ensure that the water they supply is safe and that they take appropriate measures to maintain or improve water resources. Water Utilities are also constrained by the issuing of abstraction and discharge permits by the Environment Agency. The supply of water by utilities is regulated by the Drinking Water Inspectorate (DWI) and funding and industrial practices of such bodies (within the Water Industries Act 1991) is allocated and regulated by the government regulatory inspector, OFFWAT.

2.4 Key Chronology of the Bromate Problem

A chronology of the bromate problem detailing the history of the source location, the emergence of the bromate contaminant in groundwater and subsequent investigations, monitoring and legal proceedings is provided below. The information has been compiled and summarised from information provided by the Environment Agency (Newton, 2005*b*) and a chronology provided in Hay and Buckle (2006).

1955 Planning permission granted for use of a site in Sandridge for the manufacture of chemicals.

1955-1980 The Sandridge site is operated for the production of bromine based chemicals, including bromate.

1982 The works are decommissioned, potential for contamination existing beneath the site is first discussed.

1983 Crest Nicholson Residential Ltd (Crest) purchase the factory site and adjoining land. Site investigations, including testing for potential contamination begin.

1984 Crest are granted planning permission for 30 houses and commence demolition and clearance of buildings and hardstanding from the site. The potential for bromide pollution of groundwater was assessed and high concentrations were detected on site and in downgradient groundwater samples.

1985 - 1987 Crest are granted increased planning permission for 66 houses on the site. Approval requires removal of contaminated soil to a minimum of 1m depth across entire site and locally deeper, excavations are completed by August 1986. Construction of the homes forming St. Leonard's Court (SLC) begins in November 1986 and is completed by October 1987.

1998 - 1999 VWTV detect bromate at Essendon PWS at concentration of 10.8μg/l in December 1999. The EA are informed.

2000 VWTV detect high concentrations of bromate in excess of the future drinking water standard at Hatfield PWS and immediately cease abstraction for public supply. The EA are informed and abstracted water is pumped to waste.

Sampling of upgradient locations by VWTV on behalf of the location authority lead to the St Leonard's Court site rapidly being identified as the likely source of contamination. St. Albans District Council (SADC) begin intrusive investigations at St Leonard's Court.Groundwater sampling and analysis is conducted out by various parties. Subsequent sampling by VWTV and the Environment Agency established the spatial extent of contamination and monitoring of transient changes in bromate concentrations begins.

2001 Groundwater flooding occurs in the dry valley around Sandridge. TWUL detect bromate in the Northern New River (NNR) wells in the Lee Valley and inform the EA. A Public health study is commissioned by the local health authority. Further investigations and monitoring occur in the Vicinity of St Leonard's Court and Sandridge.

2002 The monitoring network is expanded and special investigations of surface waters commenced including the Ellenbrook and River Colne. SLC is designated as Contaminated Land based upon an established pollution linkage between bromate in the unsaturated zone and the groundwater receptor and is subsequently adopted as a Special Site by the EA. The Agency begin consultation and investigation as to the determination of appropriate persons.

2003 Investigations continue, in particular relating to discharges from Arkley Hole Spring near Essendon and rising groundwater near Amwell in the Lee Valley considered to be due to decreased abstractions by TWUL, the rising groundwater is determined to not contain bromate.

2004 Bromate concentrations continue to increase at Essendon PWS and the NNR wells, threatening available water resources for public supply.

2005 Pumping trial commenced at Hatfield PWS to assess the possibility of scavenge pumping to protect downgradient sources at Essendon PWS and the NNR wells. The Environment Agency issues a remediation notice to two appropriate persons; Redland Minerals Ltd for the Bromate Contamination of groundwater, and to Crest Nicholson Residential Ltd for the Bromide Contamination of groundwater, both parties appeal.

2007 Appeals to the remediation notice are heard by public inquiry. Scavenge pumping of the Hatfield Source is promoted as an interim remediation measure and is incorporated in the Inspectors Remediation Notice. An abstraction licence is granted by the EA to VWTV for up to 9Ml/day for the purposes of groundwater remediation only.

2009 Decision is reached by The Secretary of State to uphold a modified remediation notice against Redland Minerals Ltd and against Crest Nicholson Residential Ltd, both parties apply for judicial review.

2010 The judicial review case is dismissed.

2.5 The Business Case for the Research

Bromate contamination in the aquifer presents an ongoing problem for the Environment Agency and the Water Utilities. It impacts upon their quantity and quality of available resources and as a result, direct financial and operational constraints.

2.5.1 Operational Impacts of the Bromate Problem

The legislation outlined in section 2.3 constrains the way in which Water Utilities manage groundwater abstractions and the subsequent delivery into public supply.

Water in public supply must be of wholesome quality, i.e. it must meet the standards of the Drinking Water (Water Quality) regulations for Bromate of 10μg/l at the point of consumption. Since much of the groundwater in the aquifer has concentrations at, or exceeding this concentration (see section 2.1) this has reduced the amount of water available for abstraction and increased treatment required for the remaining water.

A second major constraint is that the availability of water in the aquifer is limited, both spatially in terms of the arrangement of abstraction wells and supply network but also by the absolute volume of available water. Water Resources is further constrained by the abstraction licensing regime of the Water Resources Act and also by the Environment Agency's obligations to improve status under the Water Framework Directive. South East England is designated a "Water Scarce" region by the European Commission (European Commission, 2006) and the Colne and Lee groundwater catchments have specifically been designated of poor quantitative status under the WFD classifications. The implication is that construction of new abstraction sources or increasing existing abstractions in order to replace those lost due to bromate contamination may not be permitted, practical or cost effective.

The loss of the Hatfield PWS as a resource for public supply is the primary example of these constrains at work. The source was licensed to abstract up to 9Ml/day, which equates to the supply for approximately 50,000 consumers. Just in order to maintain supplies at present levels this water must be sourced from alternative locations. The bromate contamination represents an ongoing threat to 11 groundwater supply locations (including Hatfield PWS) with potential to migrate to others. Costs associated with the problem are likely to be incurred for as long as the pollution remains at concentrations that are hazardous. As a result of this continuing threat VWTV have undertaken measures to replace the Hatfield and Essendon sources with alternative supply boreholes located outside the affected region. The anticipated cost of closure of the existing sources and development of new sources together with the cost of associated infrastructure is estimated to be in the region of £8,000,000 and will also result in higher operational costs. There is also a need to maintain scavenge pumping to reduce down gradient concentrations to allow continued (if limited) use of Essendon. To date, all these costs have been borne by the water company and its customers, not the polluter.

Relocation of TWUL's sources is less practicable owing to a shortage of available locations and water resources. The most likely management solution for TWUL is the installation of additional treatment systems and protective measures including careful abstraction management and/or upgradient scavenge pumping to protect supplies. There are likely to be high infrastructure costs associated with this, in addition to any operational costs and the ultimate cost may be of similar magnitude to relocation of wells depending upon the methods employed.

For those wells able to remain in operation, the presence of bromate in the water requires additional water treatment prior to consumption in order to ensure drinking water quality obligations are met. The capacity of the treatment plants, seasonal and short term variation in bromate concentrations and overall abstraction licenses reduce the operational flexibility and deployable output at the remaining abstraction wells further limiting the availability of water resources. This impact is even greater in drought years when the availability of water is naturally reduced and bromate concentrations higher due to reduced dilution.

2.5.1.1 Scavenge Pumping at Hatfield PWS as an Interim Remedial Measure

In July 2005, a pumping trial began at Hatfield PWS to determine the potential influence of scavenge pumping of groundwater in order to reduce bromate concentrations in the aquifer and restrict migration of bromate to downgradient sources at Essendon PWS and TWUL's NNR sources. The aim of the abstraction was to reduce the mass of bromate in the aquifer and restrict the migration of bromate laden water to down-gradient locations east of Hatfield. The scavenge pumping has been shown to have a statistically significant effect (Fitzpatrick, 2007) with every 1Ml/day increase in abstracted volume at Hatfield PWS resulting in a $1.5 - 2.5\mu$g/l decrease in bromate concentrations at downgradient locations. Scavenge pumping also appears to interrupt the seasonal and long term rising trends and is the dominant influence on downgradient contaminant concentrations during periods of operation when compared to rainfall and other factors (Fitzpatrick, 2010).

Scavenge pumping at Hatfield PWS was promoted as an interim remediation measure in 2007 and has removed over 2000kg of Bromate from the aquifer in the period between 2005 and 2007 (Bishop, 2007). Continuation of this scavenge pumping is recommended in the Part IIA Remediation Notice issued to the appropriate persons as an interim remediation measure until a final remedial solution is identified.

Despite its success, the scavenge pumping has a number of associated uncertainties and limitations that may restrict its long term effectiveness in reducing bromate concentrations:

- Bromate concentrations are still observed at hazardous or near hazardous levels at most downgradient locations even when scavenge pumping at Hatfield is in operation.

- The volume of water that can abstracted (the maximum licensed abstraction is 9Ml/day, typical use is 6Ml/day) is constrained by the waste sewer capacity and at times of high rainfall and runoff, the capacity may be surcharged which causes an automatic cut off of the scavenging that may last for several days. However, additional natural dilution during these periods acts to reduce bromate concentrations during these periods.

- Abstracted water needs to be treated to reduce bromate to bromide, the resulting total bromide is diluted by mixing with other sewerage to ensure no impact on the receiving water.

- Hatfield is in a sub-optimum location for such pumping since it is positioned on the southern edge of the apparent extent of contamination and at some distance (6km) from the source of contamination. A more efficient location in terms of mass removed per unit volume abstraction may be achievable closer to the bromate source.

- There are financial energy and CO_2 costs associated with both operating the scavenge pumping and the additional wastewater treatment.

- The extent of bromate contamination that has penetrated into chalk porewater is a major uncertainty. The slow back diffusion of the chalk matrix might might serve to extend the duration of bromate contamination regardless of abstractions from Hatfield.

Of particular interest is how effective scavenge pumping at Hatfield PWS will be in the long term, in particular whether the apparent reduction in bromate concentrations merely represents a redistribution of the transport regime to a new steady state (following the cessation of abstractions at Hatfield between May 2000 and July 2005) and therefore the overall impact may be limited or reach a new equilibrium in the future. The likely future duration of scavenge pumping required is also of interest since there it is associated with a high operational and material cost. The cost associated with the installation of scavenge pumping infrastructure (for example the sewer diversion and additional treatment) is estimated to be around $\pounds 375,000$ and annual operational costs in the region of $\pounds 570,000$ (Bishop, 2007).

2.5.2 Financial Impacts of the Bromate Problem

These constraints all translate into financial impacts to the Water Utilities and regulatory bodies associated with the management and investigation of the bromate problem whilst maintaining water resources at quantity and quality in accordance with the respective legislation. These costs are estimated in the region of £13, 000, 000 for Veolia Water Three Valleys alone in the period 2000 - 2006 (Burns, 2007). The principal components of these costs are considered to include the following aspects:

- Drilling and investigatory work for a replacement supply well for Hatfield PWS and initial investigations for a long term replacement for Essendon PWS, estimated at some £8, 000, 000 by VWTV (Burns, 2007)
- Monitoring bromate concentrations in groundwater and surface water, estimated at ≈ £50, 000 p.a. for TWUL (White, 2007)
- Costs incurred, including legal representation and additional work relating to the Remediation Notice Appeal
- Management costs for bromate and bromide loaded water including blending to reduce concentrations, additional monitoring and other treatment aspects. Installation of Granular Activated Carbon (GAC) filtration to remove bromide at Water Treatment Works for TWUL is estimated at £50, 000, 000 with annual operating costs in the region of £2, 000, 000 (White, 2007)
- Loss of resource of the Hatfield PWS and the cost of managing scavenge pumping trials at Hatfield including the disposal and safe treatment of abstracted water. This has been estimated at some £3, 000, 000 between 2005 and 2007.
- Ongoing costs of consultants and research work undertaken to develop understanding of the problem. Monitoring

There are large costs associated with the bromate contamination and the majority of incurred costs to date has been passed indirectly to the general public, either through taxation and government funding for the regulatory bodies or through water supply bills. The total costs of these aspects are likely to continue to rise for the foreseeable future owing to the persistent nature of the problem.

2.6 Summary

Bromate is a harmful contaminant and is widespread in the Hertfordshire Chalk aquifer affecting 11 public supply wells and an area of more than $40km^2$ and although an apparent "plume" of bromate has been observed to be relatively stable between initial detection of the problem in 2000 and the present, the possibility of migration to further areas or public supply wells cannot be ruled out.

Bromate concentrations at many locations show a seasonal variation, typically being higher during summer months and low during winter month although the relative timing of the peak varies spatially and may reflect the spatial distribution and movement of recharge and its impact on water levels throughout the aquifer.

Concentrations generally show a year on year increase between 2000 and 2005 indicating that the centre of mass of the apparent bromate “plume” was changing during this period. The scavenge pumping at Hatfield PWS appears to have interrupted this rising trend in the period since 2005 and most downgradient locations have shown a decrease or stabilisation in concentrations including a dampening of the seasonal trend. However, the future effectiveness of scavenge pumping as a remedial measure is currently unknown. at Hatfield PWS appears to have interrupted this rising trend in the period since 2005 and most downgradient locations have shown a decrease or stabilisation in concentrations including a dampening of the seasonal trend. However, the future effectiveness of scavenge pumping as a remedial measure is currently unknown.

Water is a highly regulated and valuable resource, particularly in Hertfordshire where water resources are exploited close to capacity and the bromate contamination has resulted in a reduction in the availability of clean water. Future changes to the availability of water resource for example through climate change are likely to result in further stress upon water resources making finding a manageable solution to the bromate problem even more critical.

Whilst remediation notices issued under the Environmental Protection Part IIA regime may result in the offsetting of costs to monitor and manage the problem the present remediation notice does not explicitly require a clean up or a solution to the problem. Uncertainty remains regarding the future evolution of the bromate/bromide contamination in Hertfordshire and there is a clear requirement for further research in order to improve understanding and management of the problem and to reduce risks and costs associated with management options.

Chapter 3

The Hydrostratigraphy of the Hertfordshire Chalk Aquifer

This Chapter provides a description of the geology and hydrogeology of the bromate affected region of Hertfordshire in order to define the hydrostratigraphy of the aquifer, its relevant properties and to establish a conceptual understanding of the hydrogeological framework for the transport of bromate. The characterisation of Chalk stratigraphy and its relevant aquifer flow and properties was considered a required step by Watson (2004) in characterising catchment scale transport in the Chalk aquifer.

3.1 Regional Geology

The geology of the bromate affected area is indicated on the British Geological Survey sheet 239 (1978) which is reproduced from digital data in Figure 3.1. The regional stratigraphy, showing the relative age of the units, is presented in Table 3.1.

The map indicates that the Upper Chalk (mapped as the undifferentiated Lewes and Seaford Chalk) of Cretaceous age underlies the entire area except in the extreme northwest close to Harpenden where incision by the River Colne and the upper part of the River Lea has exposed the Chalk Rock (the basal member of the Lewes Nodular Chalk) and the undifferentiated Holywell Nodular and New Pit Chalk. The Chalk sequence in Hertfordshire outcrops on the southerly dipping northern limb of the east-west striking London Basin syncline and the relatively resistant Chalk (compared to adjacent softer Lower Cretaceous and Palaeocene clays) forms a line of hills known as the Chilterns. Erosion during inversion of the Anglo-Paris basin in the Palaeocene has truncated the Chalk in the Chiltern region and a warped and diachronous lower Palaeogene surface is present. Palaeocene deposits occur above this boundary and are mapped as the Reading Formation of the Lambeth Group and the London Clay Formation. These dominantly outcrop in the South and East

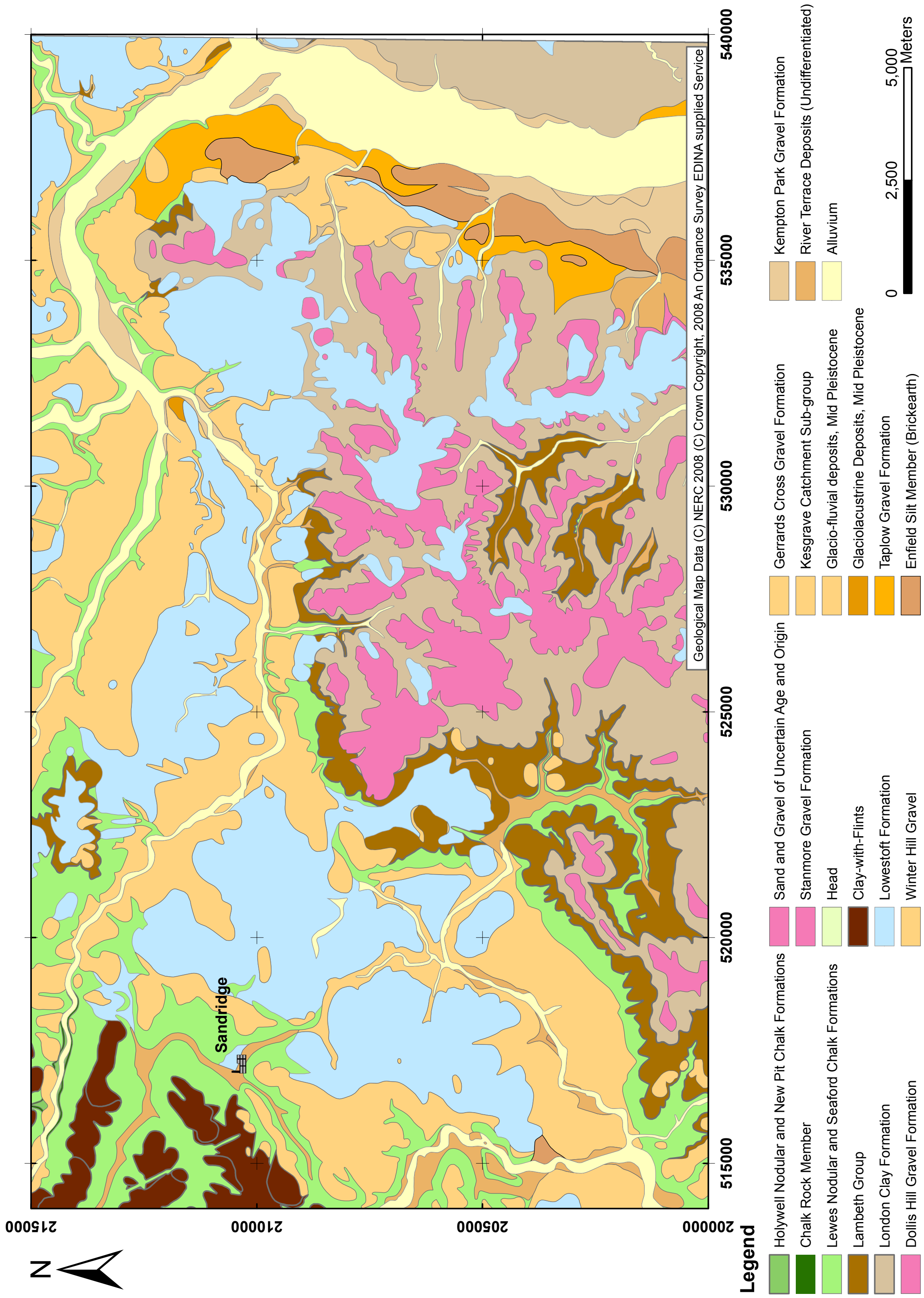


Figure 3.1: Geology of the Hertfordshire Area affected by Bromate

Table 3.1: Summary of the regional stratigraphy of Hertfordshire (After BGS, 1978)

Period	Stage	Group	Formation
Quaternary	Holocene		Alluvium Valley Gravel
	Devensian /Ipswichian		Brickearth Undivided and Flood Plain Gravel
	Wolstonian		Taplow Gravel Laminated Clay Glacial Gravel
	Pleistocene	Anglian	Boulder Clay Clay-with-Flints Pebbly Clay and Sand Pebble Gravels
Palaeogene	Eocene	Thames Group	London Clay
	Palaeocene	Lambeth Group	Reading Formation
Cretaceous	Santonian	White Chalk (Upper Chalk)	Newhaven Chalk Seaford Chalk Lewes Nodular Chalk
	Cenomanian /Turonian	(Middle Chalk)	New Pit Chalk Holywell Nodular Chalk

of the bromate affected area.

The outcrop and occurrence of drift deposits is complex, but can broadly grouped into three distinct categories.

1. Pleistocene periglacial deposits, comprising the Pebble Gravel, Pebbly Clay and Sand, and Clay-with-Flints. These occur capping slopes and hills and are likely to have been formed as periglacial in-situ weathering products during glacial periods. The Clay-with-Flints and the related Pebbly Clay and Sand occur almost exclusively in the North West of the area capping the hill tops around Harpenden. The Pebble Gravel (comprising the Dollis Hill and Stanmore Gravel as well as gravels of uncertain age and origin) appears to be related to the Palaeocene deposits and only occurs above the London Clay and Lambeth Group outcrops where it forms caps to hills in the south and east.

2. Glacial deposits associated with the Anglian Glaciation including the till of the Boulder Clay (Lowestoft Formation) and Glacial Gravel (Kesgrave Catchment Subgroup), as well as silts and lake deposits, which occur over much of the central part of the region and are dominantly associated with glaciation of the Vale of St Albans during the Pleistocene.

3. The final group of drift deposits comprises fluvial and alluvial deposits associated with the evolution of the present drainage system including river terrace deposits of the Thames, Lea and Colne as well as gravels, alluvium and flood deposits. These deposits are associated with major drainage courses and were deposited during interglacials and following the final Devensian glaciation.

3.2 Solid Geology

3.2.1 The Chalk Group

The majority of the Chalk is a pelagic sediment of Upper Cretaceous age, formed from fine calcitic fragments of coccoliths and foraminifera deposited in a warm marine sea between 200 and 600m depth (Hancock, 1975). The remaining biogenic content comprises fragments of echinoids, bivalves and other molluscs. The Chalk also contains marl and clay bands, some of which have been associated with volcanogenic ash falls, although in general, the Chalk was deposited in relatively quiet tectonically stable marine basins. Channelling, slump debris and syn-sedimentary disturbed and deformed chalks are nevertheless known to occur throughout the formation and appear to be related to local tectonic activity and areas of uplift (Mortimore and Pomerol, 1991, 1997). These disturbed features are also associated with the localised occurrence of hardgrounds (e.g. Bloomfield et al., 1995).

The Hertfordshire Chalk was deposited on the northern margins of the Anglo Paris Basin; this has resulted in condensed sequences and the development of hardgrounds and nodular phosphatic chalks is common (Hancock, 1993). Nodular chalks and hardgrounds are thought to have formed during periods of reduced deposition which allowed greater cementation of the sea floor. Bottom currents also eroded and cleared loose sediment and in some cases reworked the solid substrate, the redeposition of which formed nodular “pebble beds” (Mortimore et al., 2001). Encrustation of the exposed chalk substrate by fauna locally increased porosity of the hardground and allowed mineralisation by introduction of non carbonate minerals including glauconite and pyrite (Hancock, 1975).

The presently observed stratigraphy of the Chalk is a function of the sedimentary environment and post-depositional diagenesis and evolution of the rock. The stratigraphy of the Chalk has been shown to possess remarkably similar properties across extensive distances and a detailed stratigraphic framework has been established for the whole of the UK (Mortimore et al., 2001) which has in part been correlated with Chalk elsewhere in Northern Europe (e.g. Mortimore, 1990) and with other Upper Cretaceous sequences.

The mapping stratigraphy of the UK Chalk has been revised relatively recently (Rawson et al., 2001) and the informal divisions of the Upper, Middle and Lower Chalk have been reclassified into a formal stratigraphic group (The Chalk Group) and subset of formations. The Chalk Group comprises two sub-groups, the Grey Chalk Subgroup (approximately equivalent to the former Lower Chalk) and the White Chalk Subgroup (approximately covering the interval of the Upper and Middle Chalk).

Each subgroup consists of laterally persistent, mappable formations with distinguishing lithological and biostratigraphical characteristics (Bristow et al., 1998;

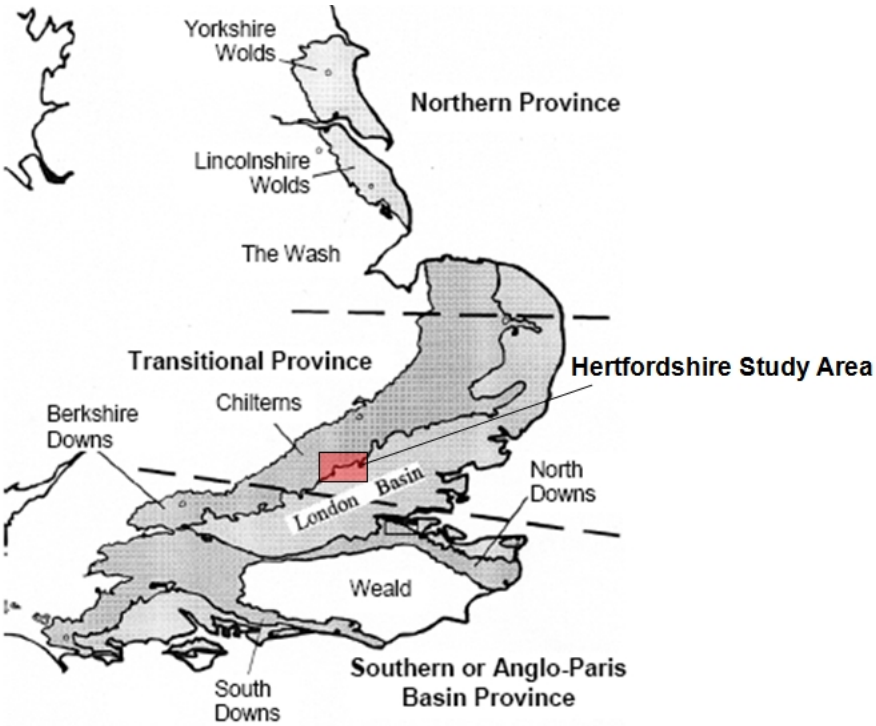


Figure 3.2: Distribution of the UK Chalk provinces (after Lord et al., 2002) and the approximate position of Hertfordshire study area (shown in red)

Rawson et al., 2001; Mortimore et al., 2001). A further informal sub-division has split the UK Chalk outcrop into three provinces distinct in terms of the lithology and faunal occurrence, these are; the Southern Province Chalk of the South Downs, North Downs and Hampshire Basin, the Northern Province Chalk of Yorkshire and Lincolnshire, and Transitional Province Chalk of the Berkshire Downs, the Chilterns and East Anglia including the Hertfordshire Chalk. The arrangement of these provinces is presented in Figure 3.2

The Chalk of the transitional province is, as its name suggests, intermediate in nature between the softer high porosity Chalks of the Southern Province and the harder more mineralised and marginal Chalk of the Northern Province and shares characteristics with both provinces. The stratigraphic formations of the transitional province are normally considered to be equivalent to those of the Southern Province (e.g. in Mortimore et al., 2001) and are considered distinct formations from those present in the Northern Province, however, further research to understand the basinal relationships between provinces is still required.

The subsurface stratigraphy of the Chalk can be established from geophysical logs, in particular those of electrical resistivity (Gray, 1958, 1965) which reflects the density and porosity of the chalk matrix, which is in itself characteristic of the Chalk stratigraphic formation. Characteristic geophysical profiles have subsequently been developed in accordance with the modern Chalk stratigraphic formations of the southern province (Mortimore, 1986; Mortimore and Pomerol, 1987). Recent studies by Woods (2003); Randle (2005); Woods (2006) have attempted to delineate the Chalk stratigraphy of the Hertfordshire area based upon characteristic features of the each formation according to their geophysical resistivity. These data are summarised in Figure 3.3 and presents the anticipated stratigraphy and thickness of the Chalk Formations in the area affected by bromate.

Geophysical logging indicates that thickness of the stratigraphic units do not greatly vary across the Hertfordshire area (Woods, 2003, 2006), however, owing to the marginal nature of the Transitional Province Chalk, local variations in the thickness and occurrence of units may occur.

3.2.1.1 The Grey Chalk

The Grey Chalk, comprising the Zig Zag Chalk Formation and West Melbury Marly Chalk formation do not outcrop at the surface in this region of Hertfordshire (BGS, 1978) and as a result, information on the nature of the Grey Chalk of the region is sparse. Where possible information has been sourced from deep boreholes or geophysical logs.

Whittaker (1921) indicates a borehole at Ware (possibly TWUL's Broadmeads PWS) penetrated approximately 50m of Lower (Grey) Chalk, and approximately 56m was penetrated at Cheshunt (possibly TWUL's Turnford PWS) in the Lee Valley. Woods (2003) indicates a tentative thickness for the Grey Chalk of the region of around 50m. Geophysical logging suggests that the upper part of the Grey Chalk, presumably representing the Zig-Zag Chalk has been encountered in boreholes at Welwyn, Wheathampsted, Harpenden, St Albans, Thundridge and Ware, generally in the north of the region although no boreholes contained identifiable marker horizons or comprised a full thickness of the formation. The Zig-Zag Chalk of the transitional provinces is pale grey to off-white and generally blocky or massive (Sumbler, 1996; Bristow et al., 1998) and at its base contains alternating marl sequences and hardgrounds (Mortimore et al., 2001)

3.2.1.2 The White Chalk Group

3.2.1.2.1 Holywell Nodular Chalk Formation The Holywell Nodular Chalk which is Upper Cenomanian to Turonian in age (dates) marks the base of the White Chalk Group and the formation is approximately 10m thick in Hertfordshire. The Holywell Nodular Chalk comprises medium hard to very hard nodular chalk with regular flaser marls. In the Chilterns the base of the formation is marked by the 'Melbourn Rock' (sensu stricto) which comprises $3-4$m of very hard weakly nodular chalkstones with traces of marl.

The upper part of the Holywell Nodular Chalk is distinguished by gritty detrital shelly chalk becoming interbedded with more marly chalks (Hopson et al., 1996; Bristow et al., 1998; Woods, 2003). The Holywell Nodular Chalk is relatively free of flint which only occurs in the highest beds although central parts of

Stage	Sub-group	Formation/Members		Key Boundary Markers	Approximate Thickness (m)
	White Chalk Subgroup	Newhaven Chalk	Peacehaven	Old Nore Marl	Presence not confirmed
Santonian	White Chalk Subgroup	Newhaven Chalk	Old Nore	Brighton Marl	Presence not confirmed
Santonian	White Chalk Subgroup	Newhaven Chalk	Splash Point	Buckle Marl	Presence not confirmed
Santonian	White Chalk Subgroup	Seaford Chalk	Haven Brow		>50m?
Coniacian	White Chalk Subgroup	Seaford Chalk	Cuckmere		>50m?
Coniacian	White Chalk Subgroup	Seaford Chalk	Belle Tout	Shoreham Marls	>50m?
Coniacian	White Chalk Subgroup	Lewes Nodular Chalk	Shoreham		34m – 40m
Coniacian	White Chalk Subgroup	Lewes Nodular Chalk	Beachy Head	Beeding to Navigation beds condensed to Top Rock series in the Chilterns	34m – 40m
Coniacian	White Chalk Subgroup	Lewes Nodular Chalk	Light Point		34m – 40m
Coniacian	White Chalk Subgroup	Lewes Nodular Chalk	Beeding		34m – 40m
Coniacian	White Chalk Subgroup	Lewes Nodular Chalk	Hope Gap		34m – 40m
Coniacian	White Chalk Subgroup	Lewes Nodular Chalk	Cliffe		34m – 40m
Turonian	White Chalk Subgroup	Lewes Nodular Chalk	Navigation		34m – 40m
Turonian	White Chalk Subgroup	Lewes Nodular Chalk	South Street	Lewes Marl	34m – 40m
Turonian	White Chalk Subgroup	Lewes Nodular Chalk	Kingston		34m – 40m
Turonian	White Chalk Subgroup	Lewes Nodular Chalk	Ringmer		34m – 40m
Turonian	White Chalk Subgroup	Lewes Nodular Chalk	Caburn	Hitch Wood Hardground	34m – 40m
Turonian	White Chalk Subgroup	Lewes Nodular Chalk	Chalk Rock	Southerham Marls	Up to 10m?
Turonian	White Chalk Subgroup	New Pit Chalk		Gun Gardens Main Marl	55m – 63m
Turonian	White Chalk Subgroup	Holywell Nodular Chalk			16m – 18m
Turonian	White Chalk Subgroup	Holywell Nodular Chalk	Melbourn Rock	Foyle Marl	16m – 18m
Cenomanian	White Chalk Subgroup	Holywell Nodular Chalk	Plenus Marls		0.9m – 1.7m
Cenomanian	Grey Chalk Subgroup	Zig-Zag Chalk		Cast Bed	22m - 28m?
Cenomanian	Grey Chalk Subgroup	West Melbury Marly Chalk	Totternhoe Stone		6.5m
Cenomanian	Grey Chalk Subgroup	West Melbury Marly Chalk			>20m?
Cenomanian	Grey Chalk Subgroup	West Melbury Marly Chalk	Cambridge Greensand/ Glaucontic Marl		<1m – 8m
				Total Anticipated Chalk Thickness	216 – 240m

Figure 3.3: Stratigraphy of the Chalk Group in Hertfordshire (Thicknesses after Woods, 2003; Randle, 2005; Woods, 2006)

the Chilterns in north Hertfordshire contain well developed flints associated with structural features(Mortimore et al., 2001). The Holywell Nodular Chalk contains a further sub-unit known as the Plenus Marls which occurs at the base of the sequence (Woods and Aldiss, 2004). These are formed from alternating greenish grey marls and marly limestone (Sumbler, 1996) and rest above an eroded unconformity on the underlying Chalk. The Plenus Marls are relatively condensed in Chilterns and are between 0.9m and 1.7m thick and probably equate with the Belemnite Marl of Whittaker (1921), are described as possessing a low hydraulic conductivity and able to generate springs by acting as an aquitard.

3.2.1.2.2 New Pit Chalk Formation The New Pit Chalk Formation is middle Turonian in age and comprises the Chalk spanning the interval approximately equivalent to the *Terebratulina lata* zone (Mortimore et al., 2001). Resistivity geophysical logs (Woods, 2003, 2006; Randle, 2005) suggest that the New Pit Chalk Formation is between 55m and 63m thick. The New Pit Chalk occurs at sub-crop throughout the study area but is only seen at outcrop in the valleys of the River Lea and River Mimram in the extreme northwest of the study area (see Figure 3.1.)

The New Pit Chalk comprises firm, flaggy to massively bedded smooth chalk with frequent well developed marl bands that provide marker horizons (Hopson et al., 1996). It is clearly distinguished from the Holywell Nodular Chalk by the upper limit of the shelly nodular chalk which is easily recognisable in sections and boreholes (Bristow et al., 1998; Mortimore et al., 2001). Flints are well developed at the base of the formation in the Chilterns but are poorly developed in the upper part (Sumbler, 1996; Bristow et al., 1998).

The New Pit Chalk is generally softer and higher porosity than the adjacent Holywell Nodular Chalk and Lewes Nodular Chalk Formations. In some areas of the Transitional Province, the upper part of the New Pit Chalk is truncated by an erosion surface indicated by hardground sequences. Channel structures in Chalk equivalent to the New Pit Chalk were identified by Ward et al. (1968) at Mundford in Norfolk.

3.2.1.2.3 Lewes Nodular Chalk Formation The Lewes Nodular Chalk Formation is Turonian to Coniacian in age and includes the Chalk spanning the interval from the Upper *Terebratulina lata* to *Micraster cortestudinariam* zones. Resistivity logs in Woods (2003) and provided by VWTV (Randle, 2005) indicate that the Lewes Nodular Chalk is 34 to 40m thick in the study area and is condensed compared to that of the Southern Province. The Lewes Nodular Chalk probably occurs throughout the area except in the extreme northwest in the valley of the River Lee and Mimram where it has been removed by fluvial erosion (see Figure 3.1).

The Lewes Nodular Chalk is a relatively coarse grained, hard and gritty nodular chalk with a sequence of well developed flints and marl seams (Mortimore et al., 2001;

Woods, 2003) although there is a reduction in nodularity across the province to the north. Frequent hardgrounds are also present and in particular two hardground sequences form the Chalk Rock and Top Rock members of the formation which are well developed in Hertfordshire (Woods, 2003, 2006).

The lower part of the Lewes Nodular Chalk contains the Chalk Rock Member which is a well developed glauconitic hardground and nodular chalk complex (Mortimore et al., 2001). The key marker horizon is the Hitch Wood Hardground at the top of Chalk Rock which is laterally persistent and is observable in core from Wiltshire to Hertfordshire (Woods, 2003; Woods and Aldiss, 2004; Woods, 2006). A prominent marl seam shown as a low resistivity spike at the base of the unit has been correlated to Southerham Marl (Woods, 2003, 2006) and acts as a secondary marker horizon. The Chalk Rock often represents a condensed proportion of the Lewes Nodular Chalk and at its thickest occurrence can represent the entire of the lower Lewes Nodular Chalk Formation (Mortimore et al., 2001). The Chalk Rock is highly variable in thickness and nature across the region (Sumbler, 1996) however, geophysical logs indicate the Chalk Rock to be laterally persistent and around 5m thick in the bromate affected area (Woods, 2003).

The "Top Rock" represents another condensed succession in the upper part of the Lewes Nodular Chalk (Mortimore et al., 2001) and is apparent on geophysical resistivity logs at Shenley, Essendon, Hertford Thundridge, Ware and Hoddesdon (Woods, 2003; Randle, 2005). It is positioned approximately 20m above the base of the Lewes Nodular Chalk and is approximately $4-5$m thick.

The boundary of the Lewes Nodular Chalk with the overlying Seaford Chalk Formation is poorly defined in Hertfordshire (Woods, 2006), diachronous in the Transitional Province and occurs chronostratigraphically above the Lewes-Seaford boundary of Southern Province (Woods and Aldiss, 2004). Due to the gradational contact (Mortimore et al., 2001) the boundary is likely to be difficult to define based upon geophysical logs alone especially where such gradation is obscured by the marls and flints that are typical of the upper Lewes Nodular Chalk and lower Seaford Chalk. Woods (2003, 2006) has tentatively assumed the boundary to occur at a low resistivity inflection above which geophysical electrical resistivity values generally decline suggesting incoming softer Seaford Chalk. The Shoreham Marl occurs close to the boundary and forms the top of the Lewes Nodular Chalk in the Southern Province succession and is thought to be correlated with a low resistivity spike close to the top of the Lewes Nodular Chalk Formation (Woods, 2003).

3.2.1.2.4 Seaford Chalk Formation The Seaford Chalk Formation comprises most of the *Micraster Coranguinum* zone spanning the Coniacian to Santonian boundary (Mortimore et al., 2001). The Seaford Chalk of Hertfordshire occurs only in the southeast of the region, and is occurs generally southeast of a line extending between Hatfield and Ware and sub parallel to the south-eastward dip of the Chalk.

To the northwest of Hatfield the Seaford Chalk has been removed by the Palaeocene transgression and subsequent erosion. Woods (2006) indicates a maximum thickness of 49m of the Seaford Chalk is present at the Hoddesdon (in the core of a syncline). It thins to the north and west, only 5m is observed at Thundridge in the north of the region and it is not observed at all at Ware. The upper part of the Seaford Chalk is considered to have been truncated by Palaeocene erosion and deposition which occurred in a generally concordant fashion with the regional dip of the Chalk. Variations in thickness of the Seaford Chalk in Hertfordshire are anticipated due to Palaeocene peneplanation, syn-depositional warping, glaciation and recent river evolution.

There is a change from the nodular hard chalk of the Lewes Nodular Chalk Formation to softer, fine grained and more massively bedded Seaford Chalk Formation (Woods and Aldiss, 2004). The Seaford Chalk is noted for its relative purity and the general absence of marl seams except for the basal sequence (Mortimore and Pomerol, 1997). Nodular beds and hardgrounds are also generally absent in the Seaford Chalk but bands of large nodular flints form the key marker bands (Mortimore et al., 2001) and are most common in the lower part of the formation where they can form large tabular and semi tabular beds (Woods, 2006), a number of mineralised sponge beds can also be identified (Mortimore and Pomerol, 1997).

3.2.1.2.5 Newhaven Chalk Formation The Newhaven Chalk Formation is Santonian to Campanian in age and spans the interval from the *Marsupites Testuradinus* to *Offaster Pilula* biozones. The Newhaven Chalk of the Transitional Province is relatively featureless and lacks many of the mappable flint horizon and marl seams typical of the Southern province (Sumbler, 1996); the Formation is also highly condensed comprising brown, flintless and possibly phosphatic chalks (Mortimore et al., 2001). The presence of Newhaven Chalk within the study area is speculated to occur but currently unproven. The Chalk of the Chilterns and London Basin was eroded during the Sub-Palaeocene transgression and the highest Chalk confirmed to be present belongs to the Seaford Member. However, as the Sub-Palaeocene transgression surface is known to be diachronous and warped (Jones, 1981) it is possible that some Newhaven Chalk may have been locally preserved, most likely within synclinal fold cores or normally faulted structures, the most likely location being the core of a synclinal structure in the region of Hoddesdon (see section 3.4) although no geophysical or core logs have confirmed this.

3.2.2 Palaeogene Deposits

Palaeogene deposits overly the Chalk above an unconformity caused by a break in sedimentation due to escalation of the late Cretaceous Alpine compression. This ultimately led to uplift and inversion of the Anglo Paris Basin and sub-aerial exposure and denudation of the Chalk in the early Palaeocene (Jones, 1981). The Alpine deformation also led to the subsidence of the London Basin as a syncline developed to accommodate the deformation. Further subsidence of the London Basin allowed deposition of a series of shallow marine, coastal and fluvial sediments (Sumbler, 1996) which onlapped onto the southern flanks of the Chiltern Chalk Hills on the northern margins of the London basin.

3.2.2.1 The Lambeth Group

The Palaeocene sediments of the Lambeth Group outcrop in the southern part of Hertfordshire where they extend in a SW-NE direction across the county. BGS (1978) mapping indicates approximately 15m of the Reading Beds of the Lambeth Group are present in Hertfordshire with a general thickening to the south. Locally the sediments have been dissected to reveal the underlying Chalk, notably on the southern flank of the Vale of St Albans by tributaries of the River Colne near Potters Bar and also in the vicinity of North Mymms and the Great Wood at Cuffley.

The Lambeth Group overlies the Chalk on a marked basal unconformity representing a complex sub-Palaeogene erosion surface that is both diachronous and multifaceted across the Weald and London Basins (Jones, 1981). The Lambeth Group in Hertfordshire is considered to be dominantly represented by the Reading Formation (BGS, 1978). The Reading Formation comprises marginal marine and alluvial floodplain deposits laid down in marshy mudflats. These dominantly comprise clay, silts and clayey sands as well as local pebble beds, channels and lenses of sand and gravel bodies (Page and Skipper, 2000).

3.2.2.2 The London Clay

A marine transgression occurred during the Eocene approximately $53-43Ma$ across the entire London Basin and much of Southern England caused by the continued subsidence and deformation of the London Basin synclinorium and the ingressing sea may have reached up to 200m in depth (Sumbler, 1996).

Up to 60m of London Clay is present in Hertfordshire, forming a relatively thin sequence compared to up to 150m present in East London (Ellison et al., 2004) and reflects the marginal basinal position of Hertfordshire as well as removal of London Clay by more recent erosion. The London Clay comprises a stiff dark blue clay with minor constituents of sand and silt and rare flint pebbles, occasionally sands and silts occur as discrete lenses and partings (Ellison et al., 2004). The clay weathers to a mid brown colour and is often fissured; the fissures can show well developed gleying. Selenite, calcareous concretions and phosphatic nodules are also all common, especially as residual weathering products.

3.3 Superficial Deposits

The superficial deposits of Hertfordshire were lain down under a wide range of depositional settings reflecting the wide variations in climate that occurred during the Pleistocene. The relationships between sediments are complex and often discontinuous, their occurrence being closely related to geomorphology.

3.3.1 Residual and Reworked deposits

The oldest superficial deposits in Hertfordshire are thought to be the Clay-with-Flints. These comprise remnant soils composed of the insoluble residue of Chalk material with a component of Lambeth group derived sediments (Lord et al., 2002) mixed by solution-lowering of the Chalk surface and cryoturbation during glacial periods. Clay-with-Flints generally comprise reddish brown clays or sandy clays with abundant gravel and cobble sized flints. Many authors (e.g. Jukes-Browne, 1906*b*; Hodgson et al., 1967) favour particularly active development in the Upper Palaeogene and warmer phases of Pleistocene but the unit may have been formed at any time since the withdrawal of the Eocene London Clay Sea. Clay-with-Flints may even be forming slowly by solution-lowering of the Chalk surface under contemporary conditions (e.g. Laignel and Meyer, 2000; Quesnel et al., 2003). The contact of the deposit with the underlying Chalk is highly irregular owing to dissolution, and foundered Clay-with-Flints deposits are often encountered infilling solution pipes and karst features in the Chalk.

The term Clay-with-Flints is often loosely used to refer to the true (*sensu stricto*) Clay-with-Flints Formation as described above but also to describe related deposits on mapping such as the Pebble Gravel and Pebbly Clay and Sand (Clay-with-Flints *sensu lato*). These comprise a heterogeneous mixture of clays, stony, clayey sands and clayey gravels derived from the solution of the Chalk and erosion and re-deposition of the Palaeogene sediments (Sumbler, 1996) and in places may have been subject to solifluction.

The BGS (1978) sheet indicates the Clay-with-Flints deposits cap the Chalk downland of the region, generally at an elevation $\geq$ 100mOD. Clay-with-Flints (*ss*) and the Pebbly Clay and Sand (Clay-with-Flints *sl*) only occur to the northwest of the bromate affected area. The Pebbly Clay and Sand appear to form as lobe shaped deposits generally at a lower elevation than the Clay-with-Flints *ss* and this may indicate that the Pebbly Clay and Sand could be derived by periglacial solifluction of the Clay-wtih-Flints and may be similar in nature to the Coombe and Head deposits of Southern England.

The Pebble Gravel exclusively overlies the Palaeogene deposits of the area and is indicated by the BGS to be of uncertain age and origin. It may be related to reworking of granular sequences of the Bagshot Sands which overly the London

Clay as well as the more recent glacial sands and gravels. Sumbler (1996) suggests that the Pebble Gravels might alternatively be related to early Thames tributary deposits.

3.3.2 Fluvio-Glacial Deposits of the Vale of St Albans

The Vale of St Albans contains deposits associated with glacio-fluvial action during the Pleistocene, including the Anglian Glaciation approximately $1,000,000 - 400,000$yBP. Engineering borehole logs, provided by Newton (2005*b*) indicate three distinct units can be recognised within the Vale of St Albans, a lower gravel, a unit of clay lodgment till (the Boulder Clay) and an upper gravel unit. The precise arrangement of the units is occasionally variable and in some cases one or more of the units are absent. The gravel units also appear to pinch out on the flanks of the Vale of St Albans.

The Lower Gravel is described as a brown sand and gravel with frequent cobbles of rounded flint and rare lenses of clay and silt. The unit also contains occasional "Bunter" pebbles of quartzite and granite derived from more distal sources (Ellison et al., 2004). Although the BGS (1978) mapping describes them as glacial gravels, three distinct stratigraphic units are described by Ellison et al. (2004) comprising the Kesgrave Catchment Sub-group, the Gerrards Cross Gravel and the Winter Hill Gravel, although only the Kesgrave Catchment Sub-group occurs in the vicinity of the bromate contamination. Rather than true glacial deposits these gravels predate the Anglian Glaciation and are thought to be deposits of the "Proto-Thames" river which passed through the Vale of St Albans prior to the Anglian glaciation (Gibbard, 1977; Baker and Jones, 1980). The lower gravels form a minor aquifer and since they lie directly upon the Chalk, the groundwater within is likely to be in communication with the Chalk groundwater. Bromate has been detected within this formation at comparable concentrations to that of the underlying Chalk (Hay and Buckle, 2006).

The Anglian Boulder Clay is a stiff brown to grey sandy clay with occasional cobbles and gravel of flint and Chalk. Locally sand, gravel and silt lenses are present and might represent channel deposits, eskers and glacial lacustrine deposits respectively and a number of different sub-units are described (Gibbard, 1977). This unit is considered to be a local aquitard and may locally confine the underlying lower gravel aquifer.

The upper gravel is described as an orange brown sand and gravel with occasional clay lenses (Newton, 2005*b*) and probably represents late-stage glacial outwash and channel deposits. Groundwater is present within this formation and has posed a construction hazard in the vicinity of Hatfield (Chilton, 1979). However, due to the presence of the underlying Boulder Clay the groundwater in the upper gravel is not considered to be in communication with the Lower Gravel unit or Chalk aquifer and it therefore represents a shallow perched aquifer; bromate has not been detected in groundwater originating from the Upper Glacial Gravel (Hay and Buckle, 2006).

3.3.3 Fluvial/Alluvial Deposits

The youngest sediments are related to post-glacial fluvial action and form a sequence of laminated clays, locally termed Brickearth, gravel sequences and alluvium comprising peat, silts and clays. These deposits are distributed across the entire area, but dominantly occur within 1km of present day river courses and are associated with deposition from surface waters. Some of these, e.g. the Taplow Gravel may be associated with the original course of the River Thames which prior to its diversion by glacial action flowed through the Vale of St Albans (Jones, 1981). Others are gravel and alluvial deposits associated with the Rivers Lea, Mimram and Colne, which are thought to have originated as Glacial outwash rivers following the southward diversion of the Thames (Sumbler, 1996).

3.4 Geological Structure

Understanding the structural evolution of Hertfordshire is necessary in order to determine the hydrostratigraphy of the bromate-affected area and the distribution of aquifer properties since the geological structure influences the arrangement of stratigraphic units, and tectonism determines the occurrence and nature of faulting and fracturing. Ineson (1962) demonstrated that underlying structure can have a significant influence on the aquifer properties of the Chalk of the London Basin, structural form has also been linked with the development of karst in the Chalk aquifer of Hampshire (Atkinson and Ingle Smith, 1974) and near Chichester in West Sussex (Robinson et al., 1999).

No structural features are indicated on the published geological map of the region (BGS, 1978), however structure contours on the base of the Upper Chalk (now part of the White Chalk Group and approximately equivalent to the base of the Lewes Nodular Chalk) are shown on the regional hydrogeological map (Cardock-Hartopp et al., 1984) and indicate a regional dip of approximately 0.5^o towards 130^oSE and slightly shallower (0.3^o) northwest of a line between Hatfield and Welwyn Garden City. A slight flexure is indicated between St Albans, The Mymms Valley and Potters Bar where the dip swings slightly east towards 126^oSE.

Minor periclinal folding and faulting as observed throughout the Chalk of southern England (Jones and Robins, 1999) is anticipated to occur locally. Fold development will influence the aquifer potential of the Chalk as it leads to fracturing, particularly along the hinge lines of anticlines; although conversely in fold cores, compression will tend to close fractures meaning that increased permeability in the hinge of a fold may be reversed with depth closer to the fold core.

A number of studies have suggested or identified evidence for minor folds in the Hertfordshire Chilterns and Northern limb of the London Basin. Wooldridge (1920) suggested that the dissolution features of the Mymmshall Brook valley are associated with a dome feature at the intersection of a NW-SE trending anticline, and an approximately perpendicular NE-SW anticline. The NW-SE feature is possibly associated with reactivation of an underlying Palaeozoic structure (The London Line) of the London-Brabant Platform (Jones, 1981). The Palaeocene deposits in this area are described as resting upon the *Micraster coranguinum* zone which is approximately equivalent to the modern Seaford Chalk Formation (Mortimore et al., 2001). However, Chalk of the *Micraster cortestudinarium* zone which is approximately equivalent to the Lewes Nodular Chalk Formation (Mortimore et al., 2001) has been recorded in a pit at Cobs Ash (Wooldridge, 1920) approximately $1.5km$ west of North Mymms. The occurrence of a Lewes Nodular Chalk in-lier within the Seaford Chalk outcrop suggests that local periclinal folding has exposed Lewes Chalk in the core of an antiformal dome in this area.

Variations in the base of the sub Palaeocene surface and the diachronous nature of this surface cross cutting the Chalk stratigraphy also suggest possible folding due to syn-depositional deformation during the Palaeocene. Contours on the base of the sub-Palaeocene surface Wooldridge (by 1920) suggest an antiformal pericline in the sub-Palaeocene surface with a fold axis aligned approximately E-W, an amplitude of approximately $60m$ and wavelength of around $3.2km$. The anticline is dome like in the region of North Mymms and extends eastwards towards Broxbourne and is considered to be associated with Chalk in-liers within the Palaeocene outcrop at Northaw and Newgate Street. Walsh and Ockenden (1982) also indicate a similar anticline-syncline pair in this area in the base of the Palaeocene consistent with that of Wooldridge (1920).

3.4.1 Evidence of Structural form from Landscape Lineaments

Lineaments (linear topographic landscape features), particularly those arising from orientation of natural drainage courses can sometimes be large scale indicators of regional geological structure and have been used to infer underlying fold, fault and joint zone characteristics. A form of landscape lineament termed a lynchet, associated with slope breaks, has been correlated with transmissivity variations in the Chalk of Northern France by Bracq and Delay (1997). Slope aspect mapping has also been used in the Chalk aquifer to identify landscape lineaments that may reflect stratigraphically and structural variations (e.g. Bonnet and Colbeaux, 1999; Bloomfield et al., 2003).

Bevan and Hancock (1986) identified NW-SE trending lineaments in the Hertfordshire Chilterns which are considered to be linked to smaller scale NW-SE trending mesofractures. A structural analysis of Hertfordshire based upon landscape lin-

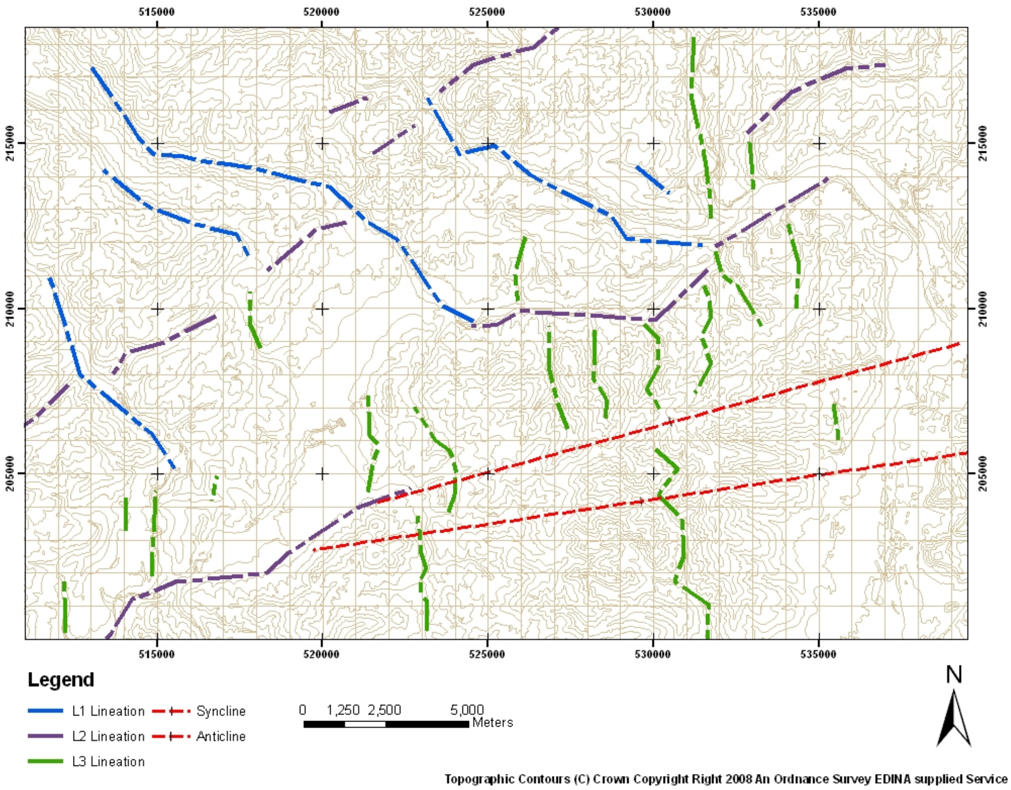


Figure 3.4: Landscape Lineaments identified in the bromate-affected area of Hertfordshire (after Bloomfield et al., 2004)

eaments (Bloomfield et al., 2004) identified 78 individual lineaments in the bromate-affected region of the Hertfordshire BGS sheet, grouped by orientation into four discrete sets (Figure 3.4).

1. The L1 lineaments shown on Figure 3.4 trend NW - SE and follow the trend of major rivers in Hertfordshire. Bloomfield et al. (2004) consider these features to comprise NW-SE striking single joints and small en-echelon faults, present throughout the Chalk outcrop which may continue beneath Palaeogene cover. These lineaments are oriented parallel to the dominant regional fabric and the orientation of large scale lineaments identified by Bevan and Hancock (1986).

2. The L2 lineaments comprise two NE-SW trending zones of linear features each $2-3$km in width and they are aligned along the approximate boundary of the Vale of St Albans and the associated Glacial deposits contained within. The northerly feature follows a line between St Albans and Welwyn Garden City. The Southerly feature generally follows the Palaeogene-Chalk contact between Colney Street and Ware. The L2 lineaments are considered to comprise gentle extensional en-echelon faulting and folding with a throw to the NW (Bloomfield et al., 2004).

3. The L3 Lineaments comprise N-S trending alignments, dominantly developed along river valleys within the Paleocene outcrop the most extensive zone trends

[t]

Table 3.2: Thickness of Chalk stratigraphic units from geophysical logs using data suppled by Randle (2005)

Formation	No. of Locations		Thickness (m)	
	Present	Full Thickness	Range	Mean
Seaford	15	0	Top not encountered	n/a
Lewes Nodular	34	8	28.1 - 51	38.2
New Pit	32	20	46 - 64	58.6
Holywell Nodular	16	13	10 - 19	15.6
Grey Chalk	16	0	Base not encountered	n/a

between Hertford and Cuffley Brook. The L3 lineaments are considered to be areas of intense fracturing, faulting and/or folding at the intersection between the L3 and L2 lineaments (Bloomfield et al., 2004).

4. The L4 Lineaments (not shown) are observed only in areas where Palaeogene cover occurs and may be linked to late Oligocene to Miocene fold axes or tectonic disturbances present in the dip slope of the Palaeogene (Jones, 1981; Bevan and Hancock, 1986).

3.4.2 Inferred Structure from Geophysical Logs of the Chalk

Geophysical logging of pumping station and observation wells in the Hertfordshire Chalk conducted by Three Valleys Water (Randle, 2005) and the British Geological Survey (Woods, 2003, 2006) provides further information on the lateral and vertical variation of the relative elevation of Chalk stratigraphy which can be used to infer structure. However, due to the discrete nature of the well logs, the origin of variations in bed occurrence and elevation cannot be distinguished between folding or faulting. Woods (2003) suggests insufficient data exist to determine the full structural form of the Chalk and estimates that over 100 data points might be necessary. Both Randle (2005) and Woods (2003) indicate that the thicknesses of the encountered Chalk formations appears to be relatively consistent across the region although formation thicknesses are condensed relative to the same succession in the Southern Province (Woods, 2006). Randle (2005, pers. comm.) has provided elevations for the base of the formations of the White Chalk group in Hertfordshire determined from geophysical logging of 53 public water supply abstraction boreholes operated by VWTV and TWUL. Table 3.2 presents the frequency of detecting each Chalk formation by geophysical logging and the range of thicknesses where the full thickness is detected. The spatial distribution of these locations is presented in Figure 3.5.

The Lewes Nodular and New Pit Chalks are the most frequently encountered and appear to comprise the main contributory aquifer units of the Chalk in the region since they are the most commonly encountered in the uncased or slotted sections of abstraction boreholes.

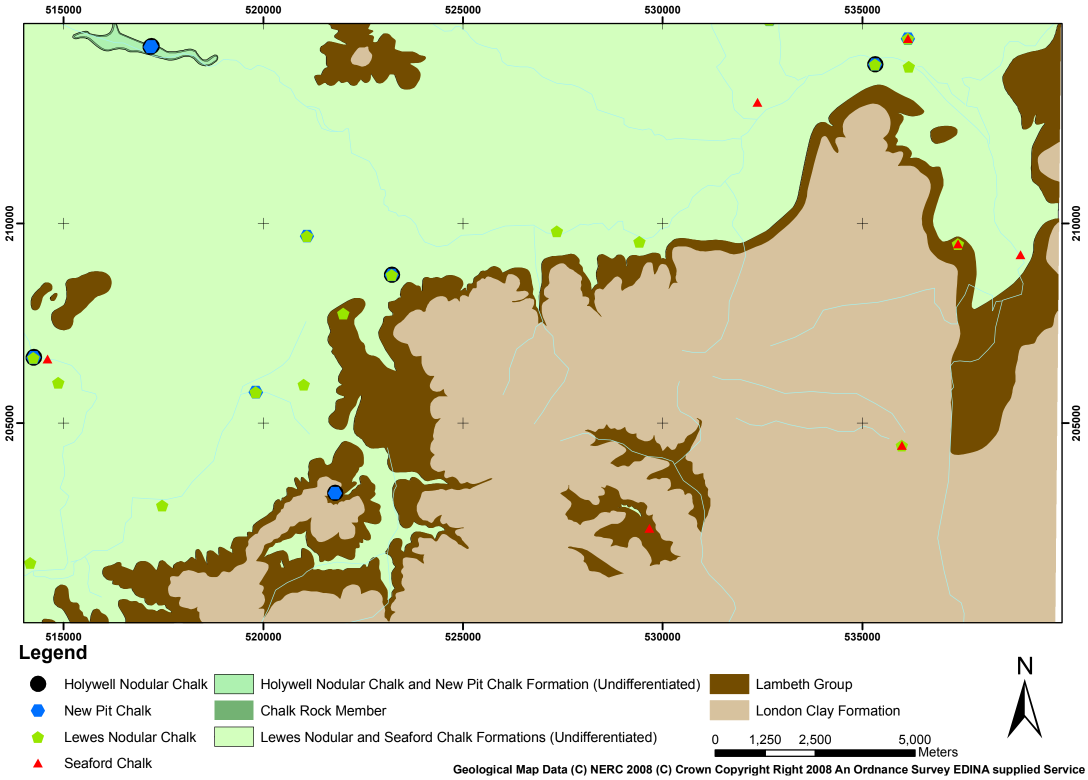
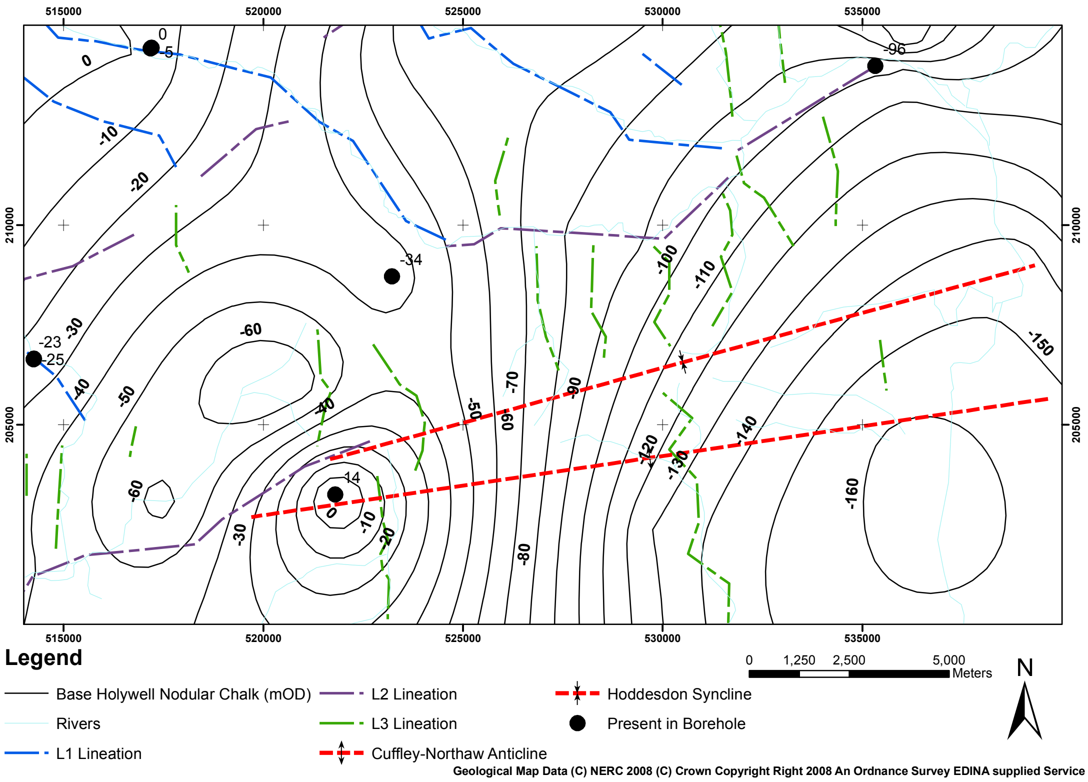


Figure 3.5: Public Water Supply Wells with geophysical logging identifying Chalk Formations

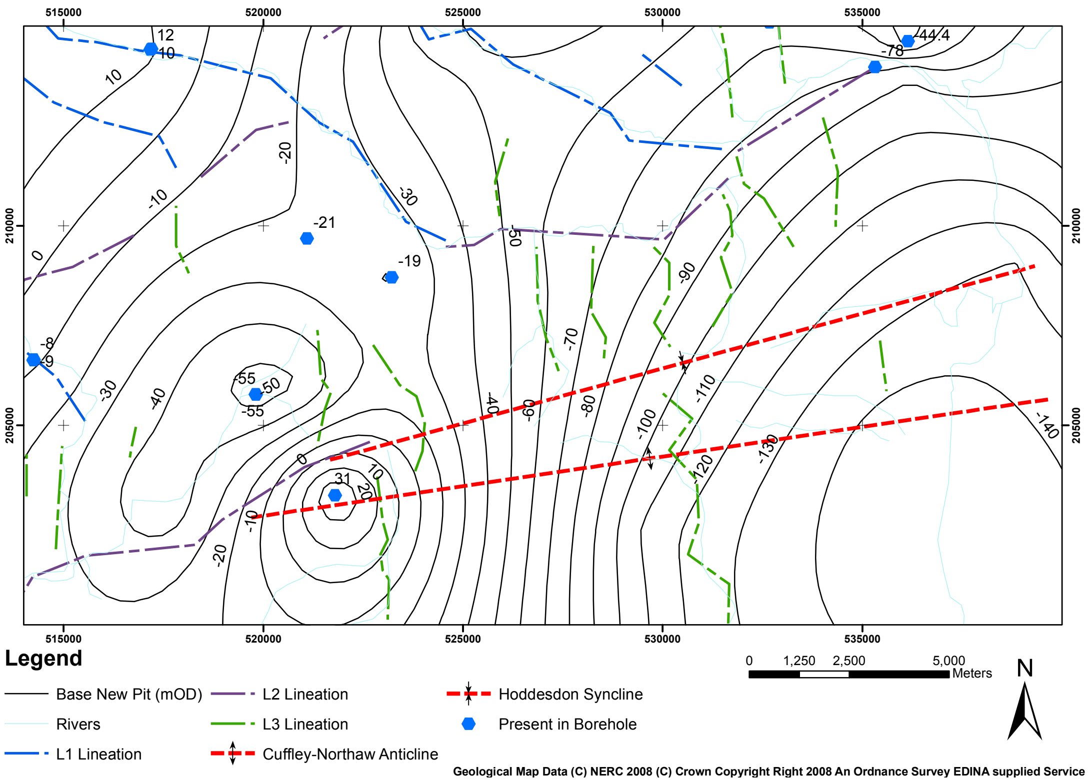
From the spatial distribution the structural form starts to become apparent and reflects the overall southeasterly dip. The youngest formation, he Seaford Chalk, is only present in PWS locations in the east and south east of the region where it also contributes to the aquifer. The Lewes Nodular Chalk is present throughout, whilst the New Pit and Holywell Nodular Chalk Formations are only present in the west and north of the region.

To further assess the structural form, the elevations of the base of each formation have been contoured by a kriging interpolation using the Surfer software package (Golden, 2009). In order to derive a full thickness dataset for each location the mean thickness of each unit has been assumed (Table 3.2). Structural contours (ignoring land surface) for the base of each formation are presented in Figure 3.6 and Figure 3.7, in addition to the structural lineations identified by Bloomfield et al. (2005) and the outcrop of the Chalk formations provided by the BGS (1978).

The south-easterly dip of the Chalk and the structural pattern is generally consistent between each formation, although this in part is reflective of the methodology used to estimate formation thicknesses. The central part of the Vale of St Albans shows the greatest variation in formation elevations, However the number of locations used to contour the data are sparesly distributed, particularly to the north of the Vale of St Albans and it is possible these variations may represent a contouring artifact rather than genuine structure particularly as the measurements available are approximately along strike from each other and there is relatively little data

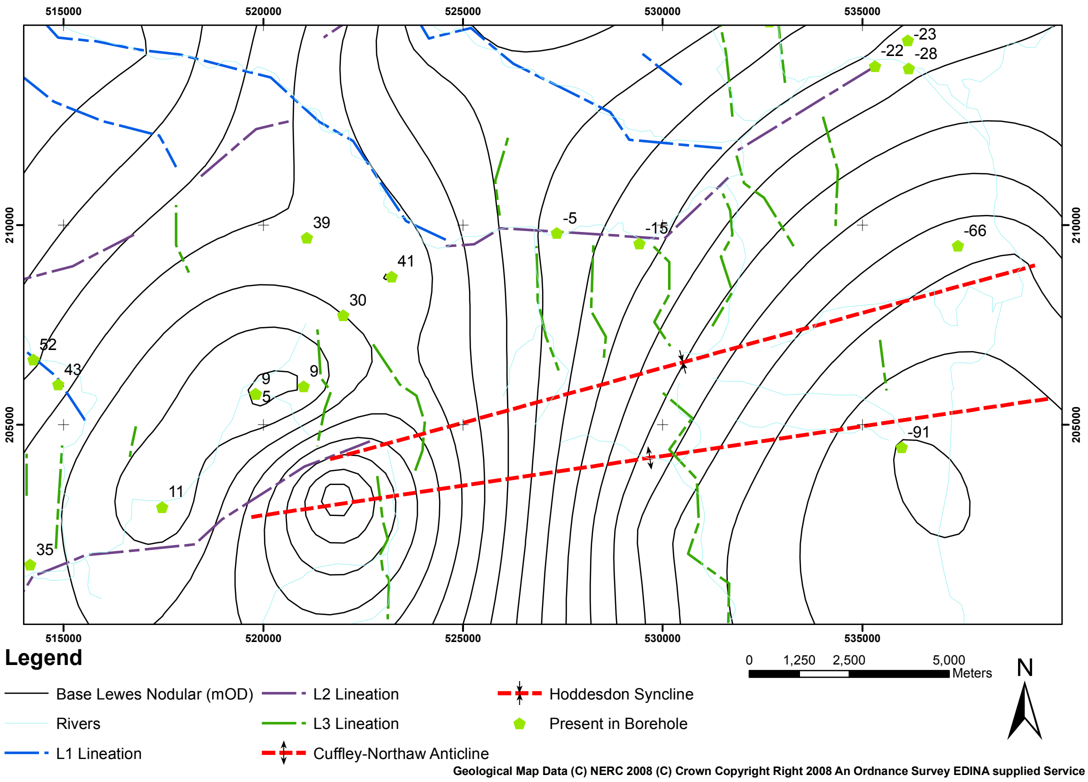


(a) Holywell Nodular Chalk Formation

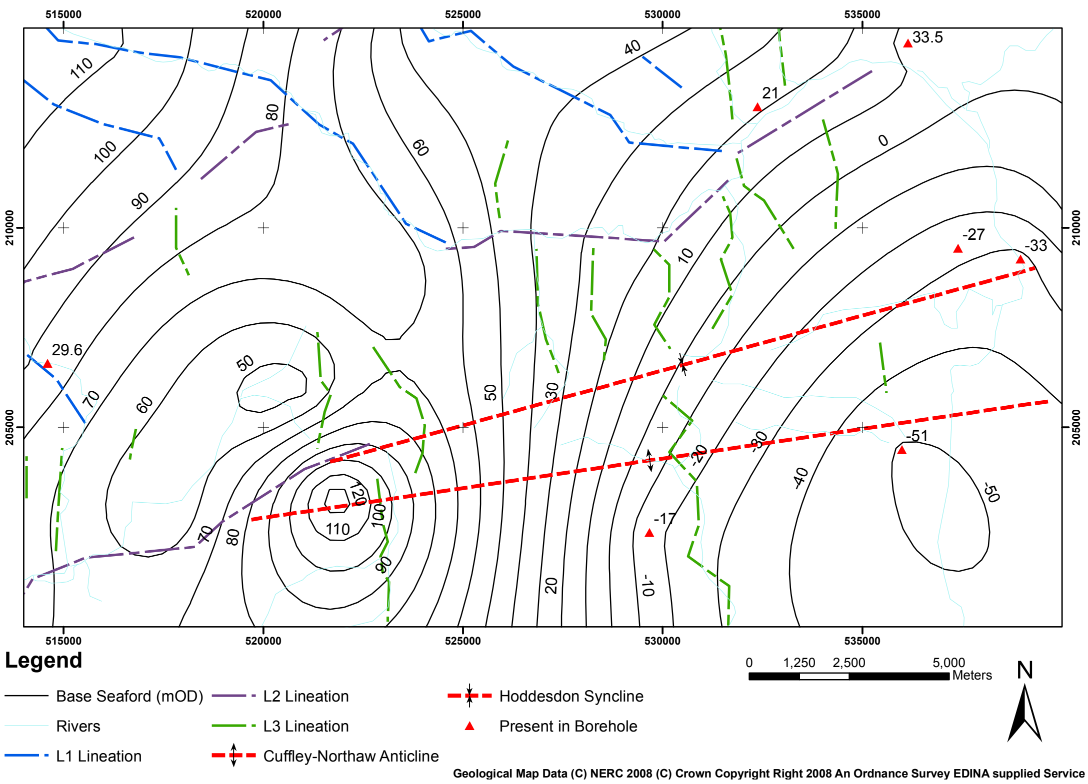


(b) New Pit Chalk Formation

Figure 3.6: Interpolated contours on the base of the Holywell Nodular and New Pit Chalk formations present in Hertfordshire, derived from geophysical logging



(a) Lewes Nodular Chalk Formation



(b) Seaford Chalk Formation

Figure 3.7: Interpolated contours on the base of the Lewes Nodular and Seaford Chalk formations present in Hertfordshire

available on Chalk stratigraphy within the area overlain by the Palaeocene.

It has been speculated by Buckle (2002) that faulting might have influenced Chalk elevation either side of the Lea valley near Hatfield or that alternatively this variation may represent an erosional unconformity in the Chalk. The arrangement of the Palaeocene outcrop forming a topographic high in the vicinity of Hatfield with Chalk outcropping in valleys either side, and the presence and intersection of several Landscape lineaments, appear to lend further support to the suggestion of faulting in the vicinity of Hatfield.

A further feature of interest is the anomalously high elevation of all formations in the North Mymms PWS abstraction borehole to the south of Hatfield. This area has been inferred from other evidence to be in the core of an antiformal structural high trending approximately E-W between Radlett and Cheshunt and the geophysical evidence further supports this. In addition, the intersection of a number of L2 and L3 lineations of Bloomfield et al. (2005) closely matches the apparent structural high and could suggest that faulting might also be significant in this area.

A possible explanation could be the presence of a series of en-echelon normal faults in this area with downthrow to the north and west both in the area of North Mymms and in the vicinity of Hatfield and that these faults are interacting with the Hoddesdon syncline and Radlett-Northaw anticline.

3.5 Geomorphology and Topography

The regional structure and tectonic history has influenced the subsequent development of outcrop patterns and geomorphological controls on landscape evolution. In turn, the denudation has influenced the distribution and characteristics of hydrogeologically significant units as well as the development of karst features in the Chalk. Thus an understanding of the landscape evolution can provide further insight into the hydrostratigraphy of the study area.

3.5.1 Geological and Geomorphological History of Hertfordshire

From the Late Cretaceous the escalation of syn-sedimentary tectonic disturbance in the Chalk, inferred from loss of marl seams and extensive development of hardgrounds (Mortimore, 1993; Mortimore and Pomerol, 1997) caused by early Alpine movements resulted in the inversion of the Anglo-Paris Basin in the early Palaeocene. Jones (1981) suggests that this resulted in rapid uplift of the Chalk and the loss through denudation of around 200m to the level of the *Miacraster Coranguinum* zone, approximately equivalent to the Seaford Chalk Formation. This sub-aerial exposure led to the erosion and solution lowering of the Chalk surface and the initial incision of drainage patterns.

Continued folding led to the gradual emergence of the present structure of the Wealden Anticlinorium and London Basin Synclinorium and later Palaeocene movements caused the subsidence of the London basin leading to deposition of the Lambeth Group above a diachronous Sub-Palaeocene transgression surface (Jones, 1981). Subsidence occurred over the period of four marine transgressions in the London Basin sequentially extending further westward before the final London Clay Transgression c.53 – 49Ma (Jones, 1981; Sumbler, 1996).

Culmination of Alpine deformation occurred during the early Oligocene (c.35Ma) (Jones, 1981) and uplift was sufficient in the Chilterns on the flanks of the London Basin to prevent any deposition of the Bagshot Beds above the London Clay within the study area. The Oligocene inversion of the London Basin led to the establishment of much of the present day drainage pattern and in particular the emergence of the early "Proto Thames".

The "Proto Thames" developed sub-parallel to the underlying geological structure in a general E-W orientation through the London Basin, however the main drainage course was further north than present and flowed along the Vale of St Albans and into the Mid Essex depression an E-W oriented trough discharging into North Sea from southern East Anglia. The depression is 3.5km in width at Hertford but widens and deepens eastward and may represent a syncline or flexure in the sub-Palaeocene surface (Baker and Jones, 1980). This phase of Thames development lasted until the first Anglian Ice advance (c. $470,000yr$ B.P.) and resulted in deposition of the early Proto-Thames river terrace deposits (Gibbard, 1977).

The Anglian Glacial advance has been inferred to have extended as far south as Watford and Finchley (Hopson, 1995) and the blocking of the Vale of St Albans by ice led to the development of an ice dammed lake which diverted the course of the "Proto Thames" southward to almost its present course and resulted in deposition of a till of Chalky Boulder Clay Till (Also known as the Lowestoft till) up to 13.7m thick at Ware and 12.8m thick south of Hertford (Baker and Jones, 1980). It is thought that the Lower Lea and Colne originated as outwash streams from the melting ice and may have carved buried valleys into the pre-glacial surface and potentially into the Chalk.

Amelioration of the climate following the Anglian Glaciation led to more extensive development of glacial outwash sands and gravels (Sumbler, 1996) and the formation of kettle holes, one of which is recorded at Hatfield. The post Anglian period was generally characterised by further fluvial development and establishment of the present arrangement of the Lea, Mimram, Colne and Thames.

3.5.2 Present Geomorphological Arrangement

The major geomorphological features of the region are indicated on Figure 3.8; three major geomorphological blocks are apparent. The Chiltern Hills in the north and

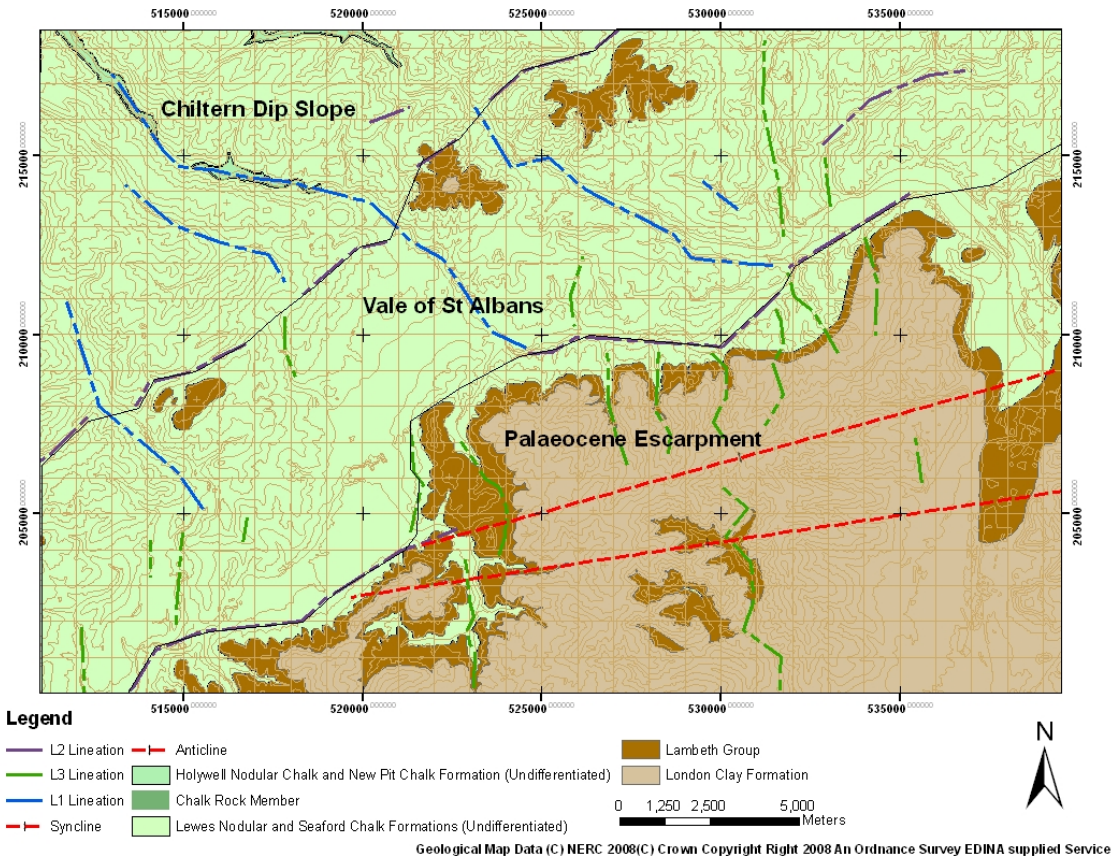


Figure 3.8: Geomorphological arrangement of Hertfordshire area affected by bromate showing major geomorphological blocks, topography and inferred structural lineaments from Bloomfield et al. (2005)

north west, the Vale of St Albans and Lee River Valley trending SW-NE across the region, and the Palaeocene Escarpment in the south of the area.

The dip slope of the Chalk of the Chiltern Hills occurs in the northwest of the area and forms a region of rolling downland. This is characterised by dry valleys with relative relief of between 30 – 75m. Major Valley Axes of the Rivers Lea, Mimram and Colne trend in a NW-SW alignment which is sub-parallel to the major structural lineation and fracture alignment (as described in Section 3.4) suggests a likely structural control of these rivers. The elevation of the valley interfluves decreases along the dip slope of the Chalk from approximately 140mOD just south of Luton to around 100mOD adjacent to the Vale of St Albans.

The Chiltern dip slopes descend into the Vale of St Albans which forms the second major geomorphological block. This is a relatively flat flat valley floor of till between 80 – 90mOD with interbedded tills and glacial sands and gravels possibly overlying early Thames gravels. It has little relative relief. The major rivers appear to cross-cut the Vale of St Albans with little change in alignment. The Vale of St Albans is between 5 and 9km wide and trends NE-SW reflecting the former course of the River Thames and the subsequent Anglian glaciation along the valley.

Along the Southern and South Eastern Boundary of the Vale of St Albans the Palaeocene deposits of the Lambeth Group and London Clay form a north facing escarpment above the Chalk outcrop. This escarpment forms low hills between 120mOD and 150mOD in elevation, described as the South Hertfordshire Plateau by Jones (1981). Drainage from the escarpment is dominantly directed northwards into the Vale of St Albans although some minor variations occur, e.g. where a pericline brings the Lewes Nodular Chalk inlier to the surface at North Mymms (see section 3.4) possibly causing the arcuate drainage form of the Mymmshall Brook. However, Wooldridge and Kirkaldy (1937) suggest that this might be related to ice damming and infilling by glacial outwash gravels of a northward drainage course towards Hatfield during the Anglian Glaciation.

Beyond the peak of the South Hertfordshire Plateau (essentially following a WSW-ENE alignment between Shenley and Hertford Heath), drainage is to the south and east. The River Lea (referred to as the River Lee beyond its confluence with the Mimram) breaches the Palaeocene escarpment at Ware and turns southward into the London Basin echoing the north-south drainage alignment developed elsewhere along the Palaeocene feather edge.

The imposed surface water drainage regime and geomorphological alignment appears to be broadly structurally concordant with the major fracture orientations and lineations identified in the Chalk. The only major exception is the discordance of River Lee turning southward at Ware rather than continuing sub-parallel to the Vale of St Albans. Jones (1981) suggests that this apparent discord is due to a N-S monoclinal axis developed along the Lee valley and exploitation by the river eroding along the asymmetric steep fold limb.

3.6 Regional Hydrogeology

The geology, geomorphology and structure of the area has direct influence upon the hydrogeological characteristics and properties of the Hertfordshire Chalk aquifer which are described in this section.

3.6.1 Regional Piezometry

Figure 3.9 shows the measured groundwater elevation for the Chalk in October 2000 for the bromate-affected area of Hertfordshire, this regional scale pattern of hydraulic head is generally consistent from year to year.

Groundwater flow into the region is dominantly from the Chalk outcrop of the Chilterns where most diffuse recharge occurs to the north west. This flow is approximately parallel to the dip slope of the Chalk and might reflect flow along both bedding parallel fractures and bedding normal fractures aligned to the main L1 fracture orientation (see section 3.4). The overall drop in head across the region is from approximately 100mOD in the northwest to around 20mOD in the Lee Valley in the extreme southeast.

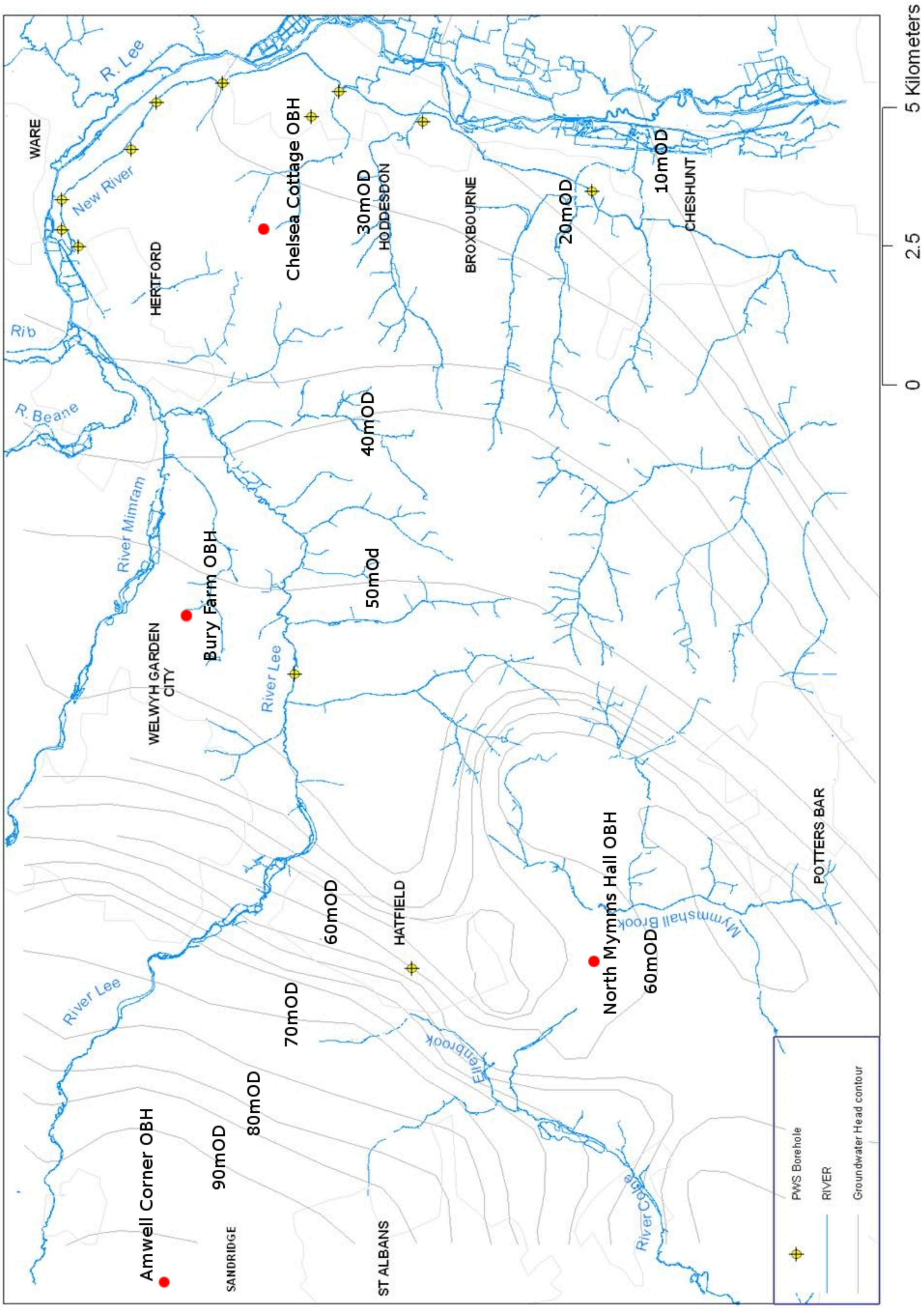


Figure 3.9: Groundwater elevations (October 2000) in the area affected by Bromate Contamination and position of representative observation wells. Contours are adopted from (Buckle, 2002).

The head contours steepen in a band approximately 4km wide just northwest of Hatfield, broadly coincident with the Vale of St Albans extending between St Albans in the southwest and Welwyn Garden City in the north. This may indicate lower permeability perhaps due to faulting or some other glacial tectonic feature. A fault, as has been inferred by Bloomfield et al. (2004) is the more likely explanation and also appears to be related to the slightly elevated topography to the west of Hatfield and might have influenced the development of the Welham Green Valley.

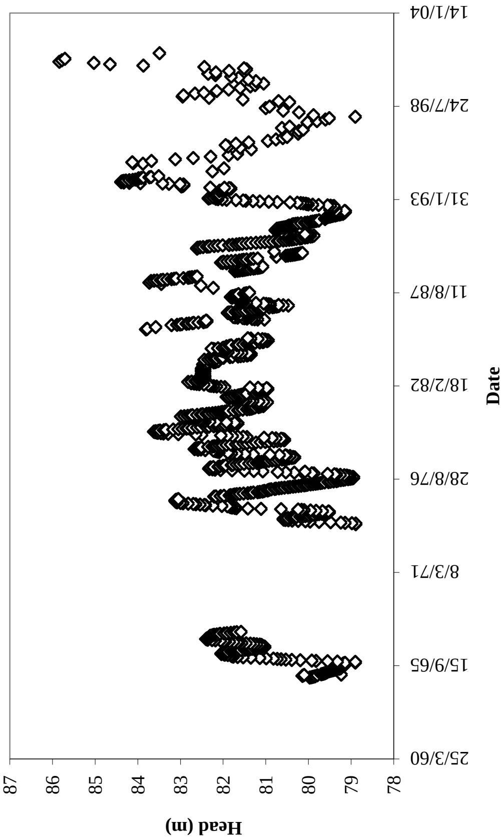
To the east of Hatfield the hydraulic gradient flattens possibly suggesting that transmissivity of the Chalk is greater and more uniform. the inferred flow directions appearing to swing approximately due east. Beyond the confluence of the River Lee with the River Mimram the contours gradually swing back toward the south east and south following the arcuate form of the River Lee into the London Basin.

A mound of relatively elevated water table exists to the south of Hatfield up to 10km in diameter and with a head of 2 to 5m above that of the surrounding Chalk. The mound is oblate in form extended in a NE-SW orientation, seasonally stable and is commonly known as the referred to as the North Mymms Recharge Mound (Buckle, 2002). The origin and influence of the mound is of considerable significance for the role of Chalk karst in the regional hydrology due to its spatial association with the catchment of the Mymmshall Brook, the high recharge being considered to be related to the presence of dissolution features in the catchment (see chapter 4). The steepest hydraulic gradient away from the mound occurs toward the southeast (≥ 0.01) however the primary flow appears to be oriented north east and it is possible that a low permeability barrier, possibly another fault, is present to the east and south east between the area of the Mymmshall Brook and Cuffley Brook (Walsh and Ockenden, 1982; Bloomfield et al., 2004).

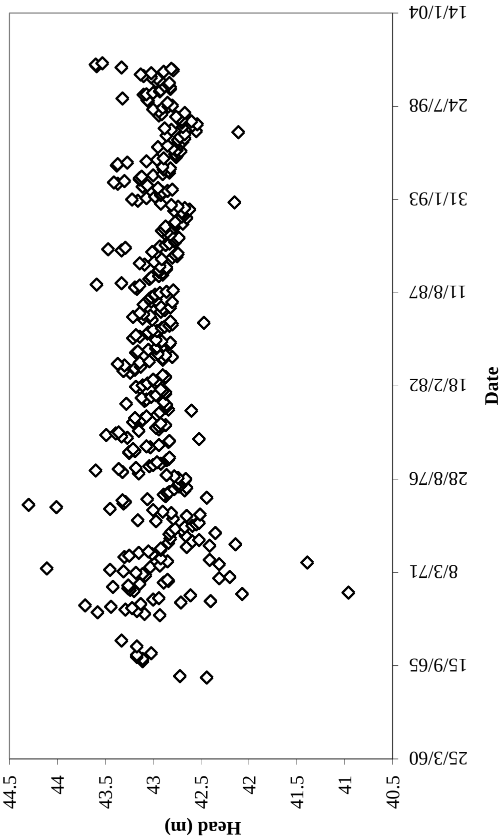
Given that the regional groundwater flow direction appears to be strongly related to dip slope drainage with superimposed concordant drainage to rivers it is possible that the Water End Swallow holes and the associated North Mymms recharge mound are related in the underlying structure of the Chalk and the structural antiformal high inferred by Wooldridge (1920).

3.6.2 Local Variations and Trends

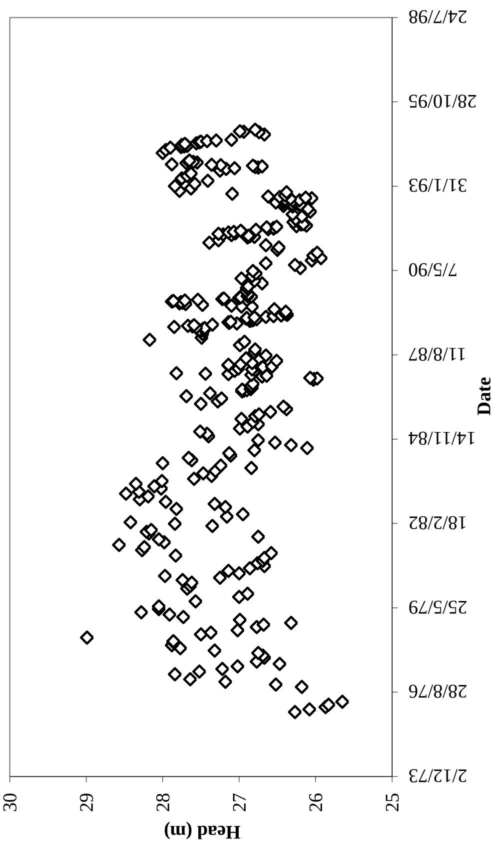
The spatial pattern of water levels is stable and shows relatively little temporal variation on a regional scale from season to season and year to year (Robinson and Buckle, 2004); however, some temporal and local trends can be distinguished. Water level data with time (raw data has been obtained from (Assem, 2005)) is presented below and can be grouped by behaviour into four regional zones broadly reflecting the geomorphology of the region, typical borehole hydrographs for each area are presented on Figure 3.10



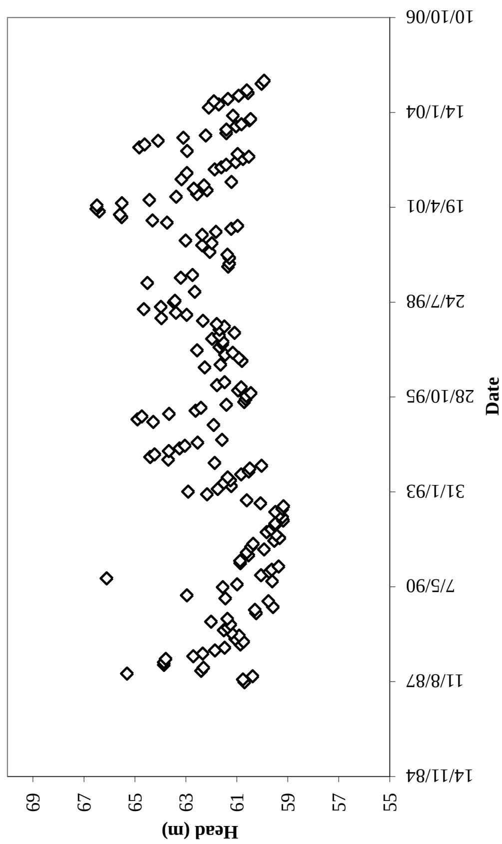
(a) Amwell Corner OBH



(b) Bury Farm OBH



(c) Chelsea Cottage OBH



(d) North Mymms Park OBH

Figure 3.10: Representative long term temporal variations in groundwater levels in the area affected by Bromate Contamination

3.6.2.1 The Chiltern Dipslope

Monitoring wells located on the Chalk dip slope in the north and west of the area show a pronounced seasonal variation in water level, probably reflecting the annual recharge distribution. Water levels reach a peak in early spring (Feb and March), receding over the spring and summer to reach an annual minimum in late summer or early autumn, usually between June and October. The amplitude of the seasonal variation is approximately $4 - 5m$, although it can be as low as 2m and as high as 15m.

3.6.2.2 The Vale of St Albans

In general, the temporal variation in water levels in the Vale of St Albans reflects that of the dip slope of the Chilterns indicating that there is relatively little discernible change in hydrogeological behaviour between the exposed Chalk of the dip slope and the drift covered Chalk in the Vale of St Albans. Minimum water levels occur in late summer and autumn between September and November with the maximum occurring in the spring between February and April, the seasonal range is between 3 and 4m slightly less than that of the dip slope which may be due to higher storage capacity provided by the overlying gravel drift.

3.6.2.3 The North Mymms Recharge Mound

Monitoring wells located in the vicinity of the North Mymms Recharge Mound tend to show a more spiky seasonal increase and recession compared to those in the Chiltern Dip Slope although this in part may be a function of the less frequent monitoring. Highest water levels are recorded in the spring, usually between January and March and lowest again between October and December, the relative annual variation is between 4 and $6m$. At North Mymms Park relatively dramatic short term variations (on the order of few days to a month) in water level can occur with a relative change in water level of up to $6m$ being recorded and suggest probably a much faster response to recharge and/or abstractions at this locations.

3.6.2.4 The Middle and Lower Lee Valley

Monitoring wells located between Hatfield and the Lee Valley tend to be positioned where Paleocene deposits overly the Chalk aquifer and the head gradients are relatively flat; and as a result these monitoring wells tend to show less seasonal variation in water level compared to further west in the catchment. Typically, the annual variation is between $1 - 2$m. The minimum water level is usually recorded between October and December, slightly later than elsewhere and can occur as late as January. The maximum water level is reached relatively rapidly and usually occurs between January and April, although given the relatively small overall variation, occasional peaks at other times including the during summer months may represent discrete recharge events.

3.7 Flow and Transport in the Chalk Aquifer

This section describes the general aquifer properties of the Chalk and the characteristics and behaviour associated with flow and transport in the Chalk aquifer. Where they are available any specific aquifer property data relating to the Hertfordshire Chalk Aquifer are described.

3.7.1 General Aquifer Properties of the Chalk

The Chalk is a dual porosity aquifer comprising a high porosity, low permeability fine grained matrix in which most of the total water content is stored, however due to small pore throats (Price et al., 1976) this water is effectively immobile under most conditions and timescales. The matrix fabric is disrupted by faults, joints and other fractures and it is these discontinuities that allow water to flow and account for nearly all of the observed effective transmissivity and aquifer properties of the rock.

One of the first large scale investigations of the Chalk aquifer properties was undertaken by Ineson (1962) based upon interpretation of aquifer pumping test data and spatial regression around pump test locations in England. These data indicated that the majority of the Chalk aquifer has a transmissivity less than approximately $110m^2/d$. The mapped data provided by Ineson (1962) suggest that for the bromate-affected area of Hertfordshire, the majority of the aquifer has transmissivity $\leq 110\text{m}^2/\text{d}$ with only localised high transmissivity between $110\text{m}^2/\text{d}$ and $220\text{m}^2/\text{d}$ developed locally around Hatfield and along the Lower Lee valley between Hertford and Cheshunt.

A general summary of the transmissivity and storage coefficients of the Chalk aquifer is provided by Allen (1997) and MacDonald and Allen (2001) also based upon the interpretation of pumping tests. Results from over 2100 measurements gave a median transmissivity of $540\text{m}^2/\text{d}$ with 25th and 75th percentiles of $190\text{m}^2/\text{d}$ and $1500\text{m}^2/\text{d}$ respectively. For storage coefficient a median value of 0.0023 with 25th and 75th percentiles of 4×10^{-4} and 0.01 respectively was obtained from 1200 aquifer tests. MacDonald and Allen (2001) note that the data are subject to locational bias since they preferentially are from boreholes and wells that have been positioned to take advantage of favourable hydraulic conditions or properties and hence may not be representative of the entire Chalk aquifer.

The data also show further locational bias, with most test data being from the Chalk of East Anglia, whilst the density of data for the Thames Basin, including Hertfordshire, is relatively low. In order to reduce bias MacDonald and Allen (2001)

Table 3.3: Summary of Chalk aquifer properties from pumping tests (MacDonald and Allen, 2001)

Area	Transmissivity (m^2/d)				Storage Coefficient			
	No.	Median	25%	75%	No.	Median	25%	75%
Chilterns	62	860	276	2100	44	0.0029	0.0008	0.028
Thames	88	230	44	990	41	0.0024	0.0004	0.0047
Hertfordshire	23	580	160	1000	23	0.004	0.0016	0.023

Table 3.4: Transmissivity values determined from pumping tests on Thames Water Utilities Ltd Northern New River (NNR) wells reported in Buckle (2003)

Source	**Transmissivity (m^2/d)**
Broadmeads	1678
Amwell End	1184
Rye Common	4000
Hoddesdon	2975
Broxbourne	1831
Turnford	1648

also examined the data on a more localised scale broadly following the provincial arrangement of Rawson et al. (2001) but subdividing the Transitional Chalk Province into the Thames, Chiltern and East Anglian regions with the bromate-affected Chalk of Hertfordshire lying approximately on the boundary between the Thames and Chiltern regions. These data are presented in Figure 3.11 and by region in table 3.3 and suggest higher overall transmissivity than suggested for the area by Ineson (1962).

MacDonald and Allen (2001) also examined the relationship between confined and semi-confined conditions and measured aquifer properties, the main difference was identified to be in the storage coefficient, as might be expected since under confined conditions elastic storage becomes much more significant. In confined conditions storage coefficient was determined to have a median value of 0.0006, compared with that of 0.008 for unconfined aquifer, the difference between the two measurements was attributed to the limited gravity drainage of the Chalk micro-porosity. Transmissivity was also found to vary between confined and unconfined Chalk with median values of $217m^2/d$ and $923m^2/d$ respectively. It was concluded that since transmissivity has a direct relationship to storativity, the properties of the fracture network dominate the observed aquifer properties and is responsible for most of the storage rather than drainage from the matrix.

The results of aquifer pumping test data carried out at 6 No. of the bromate-affected groundwater abstraction sources in Hertfordshire are reported in Buckle (2003) and are presented in Table 3.4.

These data suggest higher transmissivity than was inferred on a regional scale by both Ineson (1962) and MacDonald and Allen (2001) a possible explanation is that the transmissivity developed around a well may not necessarily represent that at some distance from the well. Close to the well permeability is often artificially enhanced by drilling fractures, acid treatment and other practices and therefore may

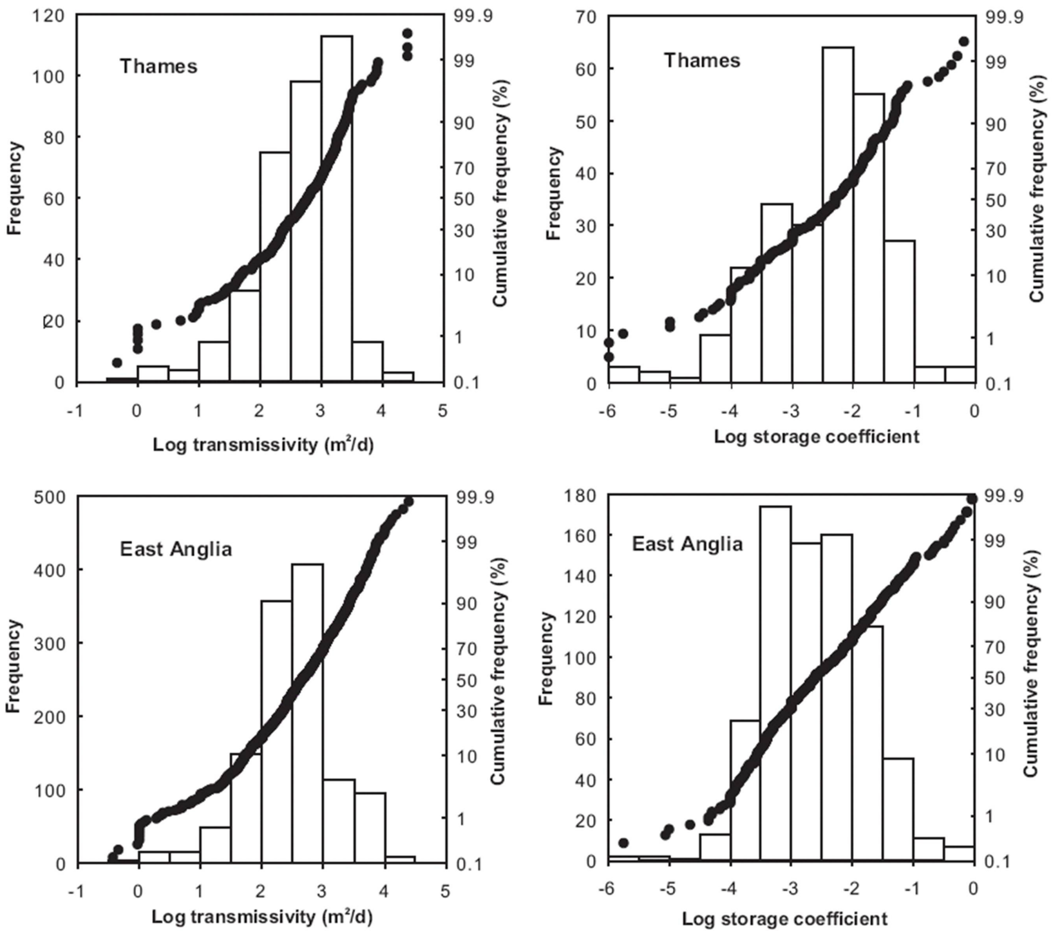


Figure 3.11: Distribution of Transmissivity and Storage Coefficient data for the Thames and East Anglia Chalk(MacDonald and Allen, 2001)

not represent that of the bulk aquifer. Moreover these data are from large abstraction wells that are likely to have been sited in positions of favourable hydraulic properties; the addition of headings and adits at many of the locations in Hertfordshire also complicates analysis. In the data presented by MacDonald and Allen (2001) and Buckle (2003) the methods used to analyse the pump test data are not described but analytical methodology can influence the calculated transmissivity. In addition, it should be remembered that unless well constrained, for example by the use of packers, pumping tests give measurements which are representative of the entire aquifer mass surrounding a well and hence they provide limited information with respect to the stratigraphic variation of flows or the geometry and distribution of the fracture network and matrix blocks in which flow occurs.

3.7.2 Characteristics of the Chalk Fracture system

Walsh and Ockenden (1982) report Chalk fracture orientations at three sites in Hertfordshire; Essendon (NGR TL283091), West End (NGR TL269091) and Castle Limeworks (NGR TL229025). All three locations showed a similar pattern of fracture orientations with a dominant NE-SW striking set and a sub-ordinate NW-SE striking set. In addition, a large proportion of fractures at Essendon showed a broad N-S alignment, which may be related to the L3 lineament identified in the area by Bloomfield et al. (2004) and indicate N-S faulting. However such N-S alignment is not seen at West End which is suggested to be broadly coincident with an L3 lineament of similar size.

Bevan and Hancock (1986) present evidence for the occurrence of NW-SE trending mesofractures in Hertfordshire which are aligned approximately parallel to the L1 landscape lineaments of Bloomfield et al. (2004) and the dominant fracture set of Walsh and Ockenden (1982). These fractures comprise vertical extension joints and conjugate steeply inclined hybrid and shear joints, the vertical joints dominate but both styles show similar dimensions of one to several metres in length and height with smooth planar surfaces. As with Walsh and Ockenden (1982) a secondary orthogonal joint set striking NE-SW is also reported by Bevan and Hancock (1986), aligned sub-parallel to the L2 lineaments of Bloomfield et al. (2004) and described as vertical or steeply inclined.

Bloomfield et al. (1995) proposed a model for the pattern of Chalk fractures in the Berkshire Chalk, which are composed of scale-invariant inclined fault-bounded blocks containing three orthogonal fracture sets, of which the fractures aligned parallel to bedding dominate. The bedding-parallel fractures were determined as having a mean spacing of 0.12m, ranging from 0.009 to 0.51m with a standard deviation of 0.13. The study also noted the NW-SE sub-vertical fracture set to have a mean spacing of 0.1m, ranging from 0.03m to 0.49m also with a standard deviation of 0.13, and a subordinate NE-SW orthogonal set as observed in other studies.

Younger and Elliot (1995) classified Chalk fractures into two groups; a bedding parallel (BP) set and a vertical bedding normal (BN) set but which also included inclined conjugate sets. The Bedding Parallel fractures are considered almost always to be sub-horizontal due to the shallow dip of most Chalk bedding in south east England. They conducted a survey of fracture frequency and geometry in the “Thames-Cambridge” area (Table 3.5) which is broadly equivalent to the Transitional Province of Mortimore et al. (2001). The data of Younger and Elliot (1995) indicate that bedding-parallel fractures are most frequent with a higher fracture frequency and longer trace lengths than bedding normal-fractures. This is in agreement with the findings of Bloomfield et al. (1995) and Jones and Robins (1999).

The data from Chadwell Spring are of particular interest as this site is located within the present study area at the north-eastern extent of the bromate plume. However, since fracture frequency is likely to be specific to the local lithological and tectonic regime in which the fractures formed, the data may not be representative of the whole study area and the values presented should therefore be treated with caution. Furthermore, owing to stress relief, frost action and other weathering the

Table 3.5: Characteristics of the Chalk fracture system (after Younger and Elliot, 1995). BN=Bedding normal, BN=Bedding parallel.

Location	Grid Ref	Chalk Group	Spacing (m) BN	BP	Distance to River (km)	Mean BN Trace (m)	Connectivity Factor (C)
Hindhay	SU868828	White	0.111	0.182	3.1	0.76	3.4
Pangbourne	SU632767	White	0.143	0.200	0.1	0.13	0.44
Playhatch	SU742765	White	0.111	0.167	1.5	0.18	0.79
Chadwell Spring	TL348135	White	0.118	0.125	0.5	0.61	2.57
Melbourn	TL380439	White	0.075	0.111	3.7	2.31	15.38
Melbourn	TL380439	White	0.100	0.154	3.7	2.82	14.1
Harlton	TL391520	Grey	0.083	0.238	2.1	0.50	2.08
Harlton	TL391520	Grey	0.167	0.167	2.1	0.35	2.88

fracture frequency as observed at outcrop may not be representative of that at depth.

CL:AIRE (2002) report fracture orientations from cores and geophysical logging by optical televiewer at a site in St Albans which show both bedding-parallel and a conjugate set of sub-vertical bedding normal fractures all striking approximately WSW-ENE. The bedding-normal set also has a subordinate direction approximately aligned WNW-ESE.

Younger and Elliot (1995) attempted to characterise the hydraulic connectivity and therefore transmissivity of the fracture system by introduction of a parameter, called the connectivity factor, C. The parameter is determined as the mean trace length of BN fractures over twice the spacing of BP fractures and is verbally expressed as *"The minimum number of pairs of neighboring BP fractures which are, on average, connected by each BN fracture"* (Younger and Elliot, 1995). However it is not clear what the relationship between connectivity factor and conductivity is in practice, and high connectivity does not necessarily result in high conductivity as aperture and fracture morphology and infill are likely to be important influences but are not included in the connectivity parameter.

Bevan and Hancock (1986) suggest that the occurrence and frequency of joints in Chalk is a function of the structural evolution and is not influenced by stratigraphy, however, the planarity, orientation and fracture roughness is stratigraphically distinct between formations. In general, higher density harder Chalk beds fracture more cleanly, producing more planar and hence more transmissive fractures. In particular, the relatively high density of the hardgrounds can lead to intense fracturing and higher overall higher conductivity (Price et al., 1977). Price et al. (1993) report that water-yielding fractures in Chalk have spacing of $7 - 12$m, but Chalk with a wider fracture spacing can still give a high yield of water.

3.7.2.1 Fracture Apertures

Fracture apertures in Chalk are difficult to determine accurately. Where encountered in-situ, outcrops are usually affected by weathering, particularly frost action which acts to enlarge fractures. In core and borehole sections disturbance during drilling can shatter the rock leading to additional fracture generation, widening of existing fractures or the infilling of open fractures. Drilling-induced fractures can be difficult to distinguish from natural fractures, particularly if the Chalk is relatively unweathered. In weathered core material, rudimentary estimates of aperture can be made from the degree of weathering or thickness of infill on the fracture surfaces (e.g. Spink and Norbury, 1990; Spink, 2002) although such methods cannot be easily validated and should be used with caution.

Younger and Elliot (1995) modelled fracture apertures in the London basin for a number of locations using ^{222}Rn isotopes in groundwater samples and found apertures to be in the range 0.01mm to 0.5mm with a mean aperture of 0.45mm. Watson (2004) presented fracture apertures based upon borehole tracer testing of between 0.37mm and 1.1mm. Bloomfield et al. (1995) suggest that fracture apertures are bimodal following two distinct distributions; fractures less than 7mm in aperture follow an exponential distribution with a mean of 1.2mm, above 7mm aperture the distribution is approximately log-normal with a mean of 11.7mm. Most other estimates of in-situ undisturbed fracture apertures fall within the range of a few hundredths of a milimetre to a few milimetres in diameter: Patsoules and Cripps (1990) give apertures of 0.1mm to 0.6mm, modelling of tracer tests by Atkinson et al. (2000) give aperture estimates of $0.29 - 0.65$mm, and Hartmann et al. (2007) suggest apertures derived from tracer tests of $0.36 - 0.38$mm.

Representations of flow in fractures typically assumes the fracture to be a planar feature of uniform aperture between two parallel faces (representing an "ideal fracture". It can be shown that the transmissivity in this case is related to the cube of the fracture aperture, following the cubic law (equation 3.1).

$$T = \frac{ga^3}{12v} \tag{3.1}$$

Where T = transmissivity, a = fracture aperture, g = acceleration due to gravity and v = the kinematic viscosity of water, taken to be $1.31 \times 10^{-6}\mathrm{m}^2/\mathrm{s}$ for Chalk groundwater at 10° C (Price, 1987). The cubic law model is therefore highly sensitive to the fracture aperture and even a small relative increase in fracture size can result in enhanced transmissivity. Laminar flow is assumed, i.e. that is flow is laminar (Reynolds number ≤ 2300) with water in contact with fracture walls being stationary. In reality, fracture aperture is likely to vary between tight and incipient fractures ($\leq$ 0.1mm diameter) to wide aperture, solution-enhanced fractures and may vary along the length and trace of a single fracture. Flow may even be concentrated into discrete channels carved into the fracture walls and roughness, tortuosity and fracture infill may all reduce the actual transmissivity of a fracture.

Assuming typical values of Chalk fracture aperture and spacing via the cubic law (e.g. Price, 1987; Barker, 1993) an estimate of the transmissivity resulting from the primary fissure component can be made (equation 3.2) where; T = transmissivity,

a = fracture aperture, g = Acceleration due to gravity, v = kinematic viscosity of water, N = Fracture Density $(1/b)$ where b is the fracture spacing.

$$K_{eff} = \frac{ga^3N}{12v} \tag{3.2}$$

The effective aquifer of the Chalk is normally considered to be the is the upper 60m below the water table (Price et al., 1993) however it is also widely recognised that the majority of open fracturing, and by result, the majority of active flow, occurs close to the zone of water table fluctuation. Taking the mean fracture aperture of Watson (2004) (0.45mm) equivalent to a fracture transmissivity of $5.69 \times 10^{-4}\text{m}^2/\text{s}$ and the mean fracture spacing of Younger and Elliot (1995) ($\approx$ 110mm) the total transmissivity of a 60m section of aquifer (containing approximately 545 such fractures) is approximately $44.7\text{m}^2/\text{day}$.

Since this result is at the lower end of the observed transmissivity values for the Chalk (see section 3.7.1) the implication is that with typically observed values, the primary fracture component alone cannot account for observed transmissivity of the aquifer (Price, 1987) and the majority of flow must be in fissures larger than those modally observed since transmissivity is proportional to the third power of the fracture aperture and that such fractures must be concentrated in a relatively narrow zone close to that of water table fluctuation. The role of calcite dissolution in enhancing the fracture size and fissure porosity of the aquifer is discussed in Chapter 4.

3.7.3 Characteristics of the Chalk Matrix

The properties of the chalk matrix are a direct consequence of the sedimentalogical setting and subsequent diagenetic evolution of the rock and the physical properties, particularly those associated with mechanical strength, have often been correlated with the bulk Chalk stratigraphy (e.g. Mortimore et al., 1990). These properties arise due to the variation in composition and texture of the matrix in terms of the coccolith species, mineralogical arrangement, and the diagenetic fabric (Mortimore and Fielding, 1990).

The White Chalk Subgroup is typically formed from $\geq 90\%$ calcium carbonate ($CaCO_3$) with a minor fraction of inorganic non-carbonate components (Hancock, 1975). The carbonate fraction is dominantly composed of micrometre sized cocollith fragments forming a biomicrite, however larger shell debris, particularly of echnoids and bivales, is relatively common and often characteristic.

The non-carbonate fraction is dominantly composed of clay minerals associated with Marl Bands, some of which are volcanogenic in origin whilst others may represent a change in sedimentalogical input and/or setting. The marl seams are laterally persistent and together with the flints form the majority of marker horizons of the aquifer. Other non-carbonate components include siliceous sponge fragments,

Table 3.6: Porosity of the Thames and Chiltern Chalk (Bloomfield, 1997)

Location	Stratigraphy	No.	porosity (%)	
			Mean	S.D.
All Data	-	2045	34	8.3
Thames and Chiltern	Upper Chalk	724	38.8	5.8
Thames and Chiltern	Middle Chalk	356	31.4	6.6
Thames and Chiltern	Lower Chalk	158	26.6	6.6

infilling of trace fossils and burrows and the mineralisation of hardgrounds by glauconite, iron sulphides and phosphate. Whilst relatively small in proportion, the non-carbonate components have influenced Chalk diagensis and the modern groundwater chemistry (Hancock, 1993). A key non-carbonate component of the chalk matrix is flint. Flints are formed during diagenesis from micro-crystalline quartz in tabular or nodular horizons usually sub-parallel to bedding, infilling burrows or trace fossils, and can also occur infilling conjugate or vertical fractures and joints.Preferential dissolution and flow can occur above and below prominent flint bands (Mortimore, 1993).

Initial accumulations of calcareous sediment led to formation of an ooze-like deposit with up to 80% porosity. Subsequent bioturbation of the sediment substrate by burrowing bivalves and echinoids reduced the porosity to around 60% (Price et al., 1993). Final burial, mechanical compaction and in the case of deep burial, pressure solution (Bloomfield, 1997) further reduced the porosity to its commonly measured range of between $30 - 40\%$ (Hancock, 1993). In some cases, particularly where post burial exposure occurred, hardground formation reduced porosity to $\leq 15\%$ (Mortimore et al., 2001). Burial and compaction also led to the formation of flaser textures adjacent to marl seams and in the Northern Province, additional tectonic compression led to low porosity Chalks (Hancock, 1975).

The Chalk porosity can also be enhanced on exhumation owing to acidic dissolution of the matrix, especially close to the feather edge of overlying acidic (humic and pyrite-rich) Palaeocene deposits. Price (1987) and Bloomfield (1997) have provided porosity data for a large number of UK Chalk samples on a regional and coarsely stratigraphic (i.e. Upper, Middle, or Lower Chalk) basis; the data for the Thames and Chiltern region are presented in Table 3.6.

The porosity of the Chalk matrix has been correlated with stratigraphy showing a general reduction in porosity with stratigraphic age, the porosity of the Lower (Grey) Chalk being limited by a higher proportion of clay minerals. Further porosity variations with stratigraphy are reported by Matthews and Clayton (1993) who plotted porosity against bio-zone (Table 3.7). Overall matrix porosity has also been directly correlated with matrix permeability (Price, 1987).

Pore-size distributions of the chalk matrix obtained by Price et al. (1976) using mercury injections on 52 samples are presented in table 3.8. The data indicate that pore throat size decreases with age and between the Northern and Southern

Table 3.7: Chalk Porosity variation with biozones (after Matthews and Clayton, 1993)

Biozone	Equivalent Formation	porosity (%)		
		Min	Mean	Max
Marsupties testudinarius	Newhaven	17	39	51
Micraster coranguinum	Seaford	16	42	50
Micraster cortestudinariam	Lewes Nodular	20	42	51
Holaster planus	Lewes Nodular	9	35	45
Terebratulina lata	New Pit and Lewes Nodular	13	38	48

Table 3.8: Pore size variations with stratigraphy and locality of the English Chalk (Price et al., 1976)

Formation	Province	Median Pore size (μm)	
		mean	standard deviation
All Chalk	n/a	0.65	0.2
Upper Chalk	Southern Province	0.65	0.14
Upper Chalk	Northern Province	0.41	0.08
Middle Chalk	Southern Province	0.53	0.14
Middle Chalk	Northern Province	0.39	0.14
Lower Chalk	n/a	0.22	0.11

Provinces. Price et al. (1976) attributed this variation to increased cementation in the northern Chalks and higher clay content in the Lower (Grey) Chalk. It was concluded that that as gravity drainage of pore spaces was unlikely due to the narrow pore throats less than 3% of the chalk matrix contributes to the effective aquifer storage and the remainder must be within the fracture system. The definition of the Transitional Province Chalk of Rawson et al. (2001) postdated this study and Price et al. (1976) assigned all samples south of Lincolnshire, including those from Norfolk, to the Southern Province Chalk.

The small grain size and pore throat size severely restricts the permeability of the chalk matrix through strong capillary forces and is the controlling factor on the hydraulic behaviour of matrix. Matrix permeability ranges between 10^{-7}m/s to 10^{-9}m/s (Price et al., 1976) and despite a possessing high storage volume due to porosity, the strong capillary forces inhibit drainage and limit the specific yield (typical values $0.01 - 0.02$) (Price et al., 1993).

3.7.4 Influence of Stratigraphy on Aquifer Properties

Lithostratigraphy has been shown to have a significant influence on the physical properties of the Chalk through sedimentary processes, diagenesis and stress changes.

Marls can influence the style of fracture development. Chalk without marl seams (e.g. the Seaford Chalk Formation) tends to form orthogonal vertical fractures. Chalk with a high frequency of marls (e.g. the Lewes Nodular and New Pit Chalks) tends to form conjugate sets. The frequency of marls also appears to influence the formation of sub-horizontal bedding-parallel joints which usually dominate, particularly in marly chalk, although sub-vertical sets can be more significant in hardgrounds (Mortimore, 1993).

The hardness and density of the matrix, and hence the overall porosity, also appears to influence the fracture style and geometry. Hardground sequences have long been recognised as being important to the aquifer potential of the Chalk since they tend to fracture more readily and more cleanly and hence can provide significant horizons for groundwater flow. The main hardgrounds of the Melbourn Rock, Chalk Rock and Top Rock are considered to have good aquifer potential (Ineson, 1962; Price et al., 1993; Mortimore, 1993). The presence of marl seams adjacent to hardgrounds as occurs in the Lewes Nodular Chalk appears to accentuate this by increasing the differential stress, since the ductile marl seams can accommodate more strain.

Marl seams and flint bands can also act more directly to control the aquifer development by restricting the vertical movement of water. Where these features are poorly fractured they can act as confining horizons and localised development of dissolution above and below marl and flints bands is commonly observed (Mortimore, 1993).

Owing to the absence of quantitative data, it is difficult to fully characterise the influence that such stratigraphic controls exert on the aquifer properties of the Hertfordshire Chalk. Even where the stratigraphy is known, such as at public supply wells, transmissivity values reflect the whole borehole and adit system and thus cannot be correlated directly to stratigraphy, particular as for those locations described in 3.4 both the Seaford and Lewes Nodular Chalk Formations are present in boreholes. At other locations in Hertfordshire, such as where borehole dilution tests have been carried out, the stratigraphy is unknown (Fitzpatrick, 2008). As a result, only relatively general conclusions about stratigraphic influence on aquifer properties, based in large part upon published literature, can be determined.

The Grey Chalk is considered to be poorly fractured although where fractures are present they are likely to comprise conjugate sets (Mortimore et al., 1990). However, the high proportion of thick marl bands and low matrix porosity is likely to lower the overall aquifer potential and limit the vertical connectivity of this unit. The alternating bands of thick marls and high density, low porosity, bands of Chalk may lead to locally confined layers or aquitards. The generally low aquifer potential of the Grey Chalk is suggested by low fracture frequency, likely small fracture aperture due to burial depth and the frequent occurrence of low permeability marl bands. Due to its depth of occurrence, the Grey Chalk is rarely encountered in boreholes; on this basis it is considered that the Grey Chalk is unlikely to contribute to the Chalk aquifer potential or water resources of the bromate-affected area of Hertfordshire.

The Holywell Nodular Chalk is encountered at depths below 100m in public supply wells at which the contribution of flow from open fractures in the Chalk is considered to be relatively minor; hence the Holywell Nodular Chalk is not considered to be a significant aquifer unit in the bromate-affected area of Hertfordshire. However the presence of the hardground unit forming the Melbourn rock is indicated at Turnford PWS and Bromate PWS on construction drawings (in Buckle, 2005) and was indicated with minor springs and sand-filled open fissures at Turnford PWS. The Melbourn Rock is recognised as an important contributory aquifer unit in Hertfordshire (Ineson, 1962) since due to its high density, hard mineralisation and low porosity matrix it fractures readily and cleanly into conjugate fracture sets (Mortimore et al., 1990). However, the proportion of flow derived from the Melbourn Rock, and their bromate content in the contaminated region remain uncertainties in the absence of quantitative data or depth sampling from this horizon.

The New Pit Chalk is considered to be a contributory aquifer unit in Hertfordshire being encountered in the majority of Public supply wells in the region at depths between 40-100m and thus within the likely zone of the effective aquifer. However, little quantitative information is available regarding the nature of the New Pit Formation in Hertfordshire especially with regard to its likely aquifer properties. The matrix of the New Pit Chalk is generally reported as a medium hard unit with intact dry density in the range 1.48 to 1.79Mg/m^3 (Jones and Robins, 1999; Lord et al., 2002) equating with a porosity of $32\% - 44\%$. The New Pit Chalk of the Southern Province typically shows widely spaced (600mm-2m) conjugate fractures (Mortimore et al., 1990).

The typical nodular and marly nature of the Lewes Nodular Chalk suggests that inclined conjugate joints are likely to dominate rather than normal vertical jointing due to the variation between competent brittle and more ductile marly units and the control of marl seams on fracture propagation as suggested by Cooke et al. (2006). Mortimore et al. (1990) indicate the Lewes Nodular Chalk of the South Downs is typified by widely spaced (600mm - 2m) conjugate joints and Younger and Elliot (1995) recorded 0.12m fracture spacing for both bedding-normal and bedding-parallel fracture sets for relatively unweathered buried Chalk probably belonging to the Lewes Nodular Chalk.

In terms of hydrogeological behaviour, it is appropriate to consider the Chalk Rock member separately form the Lewes Nodular Chalk Formation. The Chalk Rock forms a condensed sequence of hardgrounds and nodular chalks and whilst similar in nature to the whole of the Lewes Nodular Chalk the hardgrounds are much better developed. The hardgrounds and highly nodular beds of the Chalk Rock are likely to possess high density, tend to be brittle and hence likely to be more intensely fractured (Jones and Robins, 1999) and more cleanly fractured (Price et al., 1993) with a larger fracture aperture. The resulting high density of hardgrounds means that the Chalk Rock forms a separate hydrostratigraphic aquifer unit of lower porosity. The porosity of the Chalk Rock is indicated by Bloomfield et al. (1995) to be in the range $10 - 15\%$ at Winterbourne and $5 - 10\%$ at Faircross, both sites

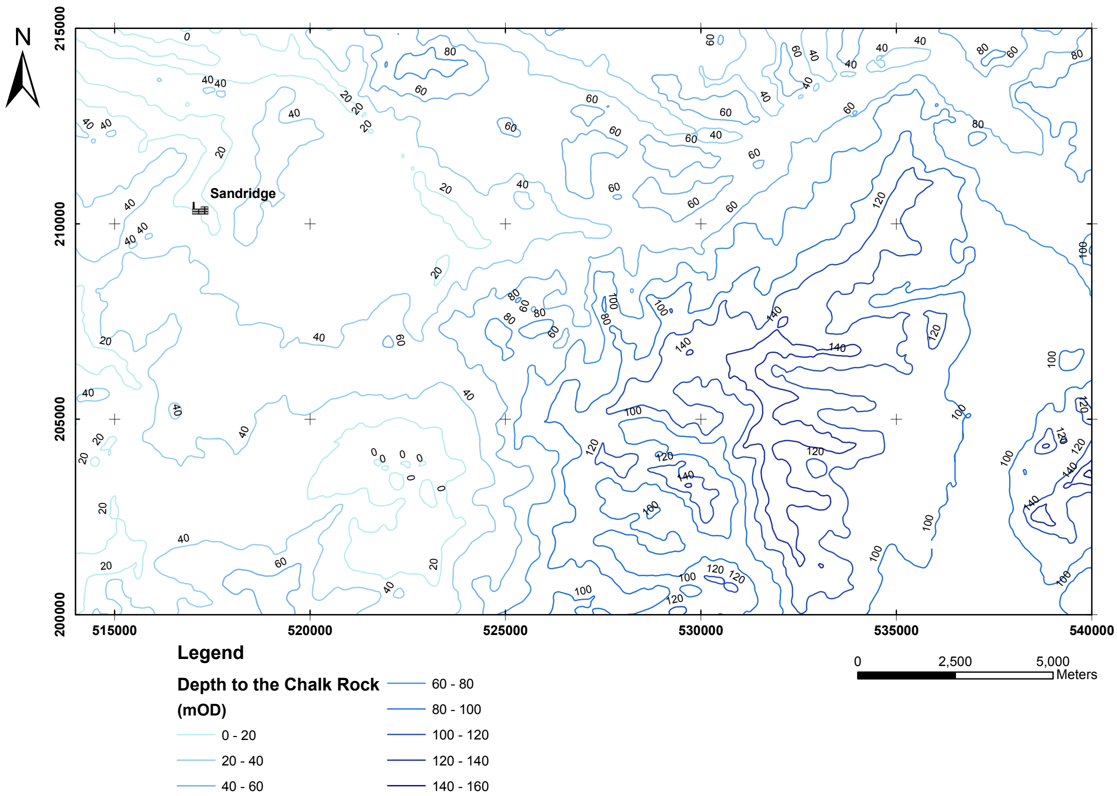


Figure 3.12: Inferred depth to the Chalk Rock based upon interpolation of a 200m grid Digital Terrain Model with contours on the base of the Lewes Nodular Chalk. The Chalk Rock is assumed to be 15m above the Base of the Lewes Nodular Chalk Formation.

are in Berkshire in the Transitional Province where the Chalk Rock is considered to be best developed. Increased fracture prevalence and aperture is evident and Ineson (1962) notes that the Chalk Rock is a major aquifer contributory unit in Hertfordshire and should always be penetrated in wells if possible.

The high aquifer potential of the Chalk Rock is further illustrated in geophysical well logs from the region (Randle, 2005). The Chalk rock is clearly defined by a broad high resistivity peak, the main marker horizon being the Hitch Wood Hardground. The Chalk Rock Member is approximately 4-5m thick in the region and is exploited the construction of adits and headings at Essendon. Flow logging also indicates inflows close to the Chalk Rock interval at Essendon PWS, Tyttenhanger PWS, Roestock PWS and Hatfield PWS; caliper logs indicate the occurrence of borehole widening associated with Chalk Rock at Tyttenhanger PWS and Hatfield PWS.

Interpolated structural contours show the base of the Lewes Nodular Chalk (Figure 3.6) to be approximately 15m below the elevation of the Chalk Rock (Woods, 2003). The approximate depth to Chalk Rock is presented in Figure 3.12, using a 200m grid digital terrain model.

The interpolated contours show a close match to the mapped outcrop of Chalk Rock in the Upper Lee Valley lending confidence to the method. Following the regional structure the Chalk Rock increases with depth toward the east. The unit is generally shallow and within the probable zone of the effective aquifer ($\leq$ 60mbgl) across the north and west of the area, the 60m depth contour being approximately coincident with and sub-parallel to the Palaeocene Feather Edge. Additionally, the Chalk Rock is at a relatively shallow depth ($\leq$ 20m) in the vicinity of the bromate source zone at Sandridge and could be an important transport horizon, as was speculated by Hay and Buckle (2006). The Chalk Rock is also at a relatively shallow depth in the area of the Mymmshall Brook and along the Palaeocene Feather edge, approximately coincident with the zone of karst development. It is possible that the wide aperture, clean fractures associated with the Chalk Rock could be being exploited by preferential dissolution and karst in this unit. It is also generally considered (e.g. Price, 1987; Price et al., 1993) that bands of hard grounds such as the Chalk Rock can still be important units for groundwater flow at greater depths than normally considered due to their higher fracturing and greater compressive strength which resists fracture closure.

The Seaford Chalk formation is the dominant aquifer unit in the Chalk of the South Downs (Jones and Robins, 1999) and has a relatively high matrix porosity. Typically in Seaford Chalk bedding-normal fractures dominate and are orthogonal and medium spaced (200-600mm) Mortimore et al. (1990). Geophysical investigations in the South Downs have indicated that the Belle Tout Marl and associated hard beds of the Seaford Chalk Formation are important flow horizons (Jones and Robins, 1999). Flow has also been associated with localised fracturing and karst development adjacent to the Seven Sisters Flint in the South Downs of Sussex, Hampshire, the North Downs of Kent (Watson, 2004) and Northern France.

Mapping by the BGS does not differentiate between the outcrop of the Lewes Nodular and Seaford Chalk Formations in Hertfordshire, however since these formations reflect the main aquifer units in the region and have been demonstrated to posses different stratigraphic and hydraulic characteristics, determining the spatial distribution of each formation is necessary to better characterise the hydrostratigraphy of the aquifer. To investigate the possible outcrop of the Seaford Chalk Formation the structural contours determined for the base of the formation have been intersected with a 200m gridded digital terrain model (DTM) of the region using GIS. The inferred boundary (Figure 3.13) is consistent with reported field observations, in that it does not intersect the outcrop of the Chalk Rock, and also occurs at higher elevation and further to east than the base of the Lewes Nodular Chalk and Chalk Rock. In addition, the contours also indicate that Lewes Nodular Chalk should outcrop in the vicinity of North Mymms in accordance with the bio-stratigraphic evidence of Wooldridge (1920).

This suggests that across the majority of the region the Seaford Chalk is the formation present at outcrop, however, particularly in the north and west it is likely to be fairly shallow as most geophysical logs indicate that the Lewes Nodular Chalk is the primary aquifer unit except in the East around the Lee Valley. The Seaford

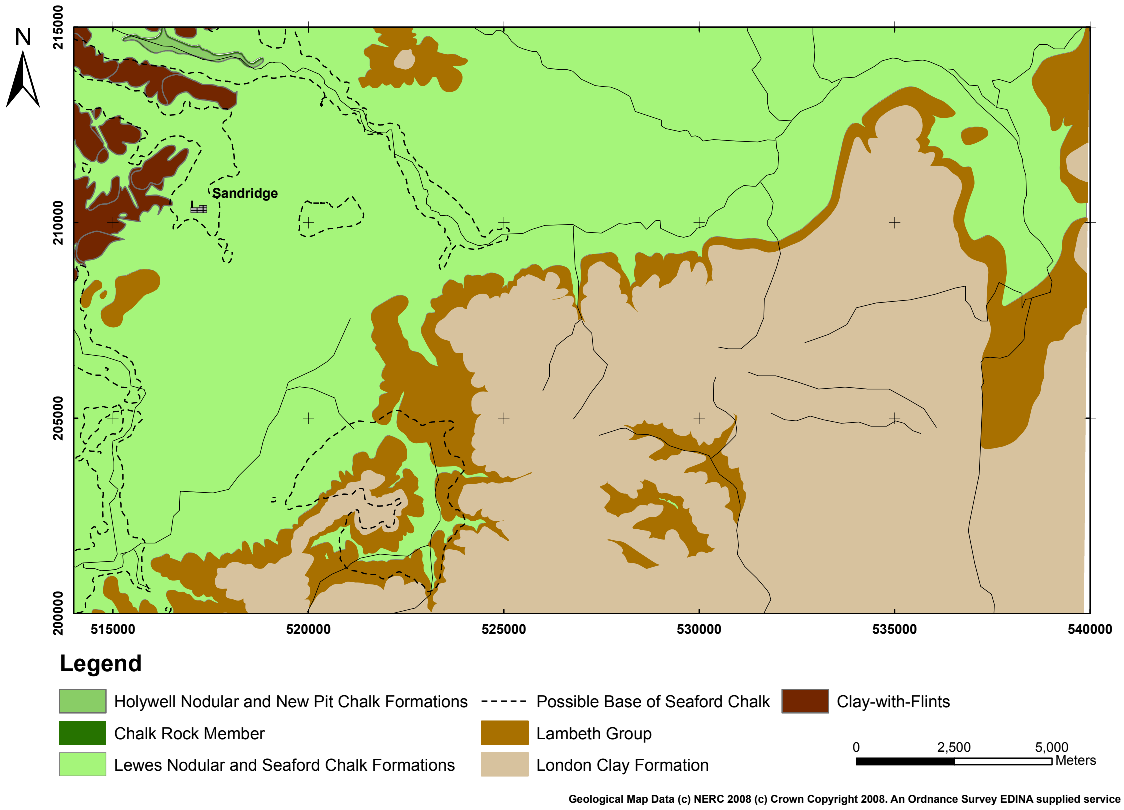


Figure 3.13: Inferred boundary (dashed) of the Seaford and Lewes Nodular Chalk Formations

Chalk has been removed in the dry valleys of the Chiltern Dip slope and the valleys of the River Ver, Lea and Mimram in the north and west of the region. This further suggests that the bromate source at Sandridge is located within the outcrop of the Lewes Nodular Chalk.

It should be noted that both the depth to the Chalk Rock and Seaford Chalk boundary presented here are intended to be indicative rather than exact since there is uncertainty associated with structural form and contours (as described above) as well as limitations of a 200m grid interpolation spacing on elevation data in the digital terrain model. In addition, this estimate does not take into account any differential erosion of the Seaford Chalk that might have been caused either by the Palaeocene transgression or by deposition of drift deposits, including the Clay-with-Flints and Vale of St Albans Glacial deposits, the occurrence of which is close to the inferred Seaford Chalk boundary.

3.7.5 Influence of Geomorphology on Aquifer Properties

The geomorphology of the Chalk aquifer at outcrop has long been considered to be indicative of the likely aquifer properties and potential, born out by the siting of many abstraction locations of Victorian age along or adjacent to rivers and within river valleys. More recently, the relationship between aquifer properties and the surrounding geomorphology has been investigated more quantitatively (e.g. Ineson, 1962; Foster and Milton, 1974; MacDonald and Allen, 2001)

The statistical investigation of Ineson (1962) indicated a strong association of relatively high transmissivity and valleys (comprising both active surface drainage and dry valleys). In particular the Rivers Colne, Lea and their tributaries in Hertfordshire were described as areas of high transmissivity and Ineson (1962) speculated that this might reflect some underlying structural fabric in the Chalk such as increased fracture frequency which has been exploited by both surface water drainage and groundwater flow. One possible origin may be differential loading due to reduction in overburden thickness in valleys leading to stress relief fractures and heave. Younger and Elliot (1995) suggest that the enhanced aquifer properties of Chalk valleys is due to the preferential dissolution-enlargement of fractures near rivers, rather than an increase in fracture frequency since they were unable to correlate fracture frequency with distance from rivers, however, their study did not consider the spatial relationship of fractures to dry valleys which are also considered to be linked with zones of high transmissivity. MacDonald and Allen (2001) also investigated the relationship between river valleys, interfluves and transmissivity for the Kennett Valley, and found only a weak correlation.

The present-day geomorphological arrangement of valleys in the Chalk outcrop of Hertfordshire does appear to reflect the underlying structural fabric of the Chalk as described in Section 3.4: The Ver, Lee and Mimram valleys all appear to be aligned sub-parallel to the dominant fracture lineation and L1 Landscape lineaments of Bloomfield et al. (2004), all of which are sub-parallel to the direction of the hydraulic gradient. The Vale of St Albans is aligned sub-parallel to the secondary fracture direction, along the strike of the Chalk bedding and sub-parallel to the L2 Lineation of Bloomfield et al. (2004).

Chalk valleys are often associated with the development of head, coombe deposits and deep weathered profiles caused by a combination of solifluction, cryoturbation and in-situ weathering particularly during glacial and peri-glacial periods. The presence of these deposits and weathered profiles is considered (e.g. Younger, 1989) to lead to a low permeability cap at the surface of the Chalk in valley areas and when recovered in boreholes is often referred to as "putty chalk" due to their low density and ability to become thixotropic to a chalk slurry or putty when disturbed (Waltham, 2002). As a result the term "putty chalk" can often be misleading particularly as relatively intact and unweathered chalk can still be recovered as putty chalk due to poor drilling technique.

A better terminology is the "Structureless Chalk" description of Spink and Norbury (1990) and (Spink, 2002), which more appropriately describe the weathered characteristics. Two end members of structureless chalk are recognised:

1. A clast supported chalk rubble, the clasts of which may retain some of the original rock fabric and are separated by a comminuted chalk matrix.

2. A matrix supported structureless chalk, dominantly formed from a comminuted and weathered chalk, predominantly silt sized particles but may contain a lesser proportion of Chalk and flint rubble.

Various formal descriptive schemes for weathered chalks have been developed (e.g. Ward et al., 1968; Spink and Norbury, 1990; Spink, 2002) but all share in common a number of defining characteristics, the intact strength of the chalk matrix, the spacing and aperture of fractures and the presence and nature of the fracture in-fill. These characteristics are likely to be highly site-specific that hydraulic conductivity testing revealed it did not vary linearly with the depth of weathering in Chalk (Price et al., 1979, in (Price, 1987)).

Due to partial re-cementation, matrix-dominated structureless chalks probably possess similar characteristics in terms of porosity and hydraulic conductivity to the unweathered chalk matrix with a permeability in the range $10^{-7} - 10^{-9}$m/s. Given the more rubbly nature of the clast-dominated structureless chalk, hydraulic conductivity would vary depending upon the relative proportions of comminuted chalk matrix and rubble. Preferential rapid flows have been observed in clast-dominated structureless chalks (e.g. Price, 1987). Younger (1989) also speculated that cryoturbation of chalk rubbles in valleys might have led to development of enhanced fissure porosity and thus increased permeability.

The presence of “putty chalk” (probably referring to matrix dominated structureless chalks) within the Sandridge dry valley (Robinson and Buckle, 2004) in and around the bromate source zone has been thought to act as a low permeability barrier to the downward and lateral movement of bromate in the Chalk unsaturated zone and hence might have influenced the release of bromate to the groundwater. However, as has been described above this may not reflect actual ground conditions and should be treated with caution. The other location at which the depth of weathering and development of structureless chalk may affect transport is at the interface of the Chalk and overlying fluvio-glacial deposits of the Vale of St Albans.

3.7.6 Interaction of the Fracture and Matrix Components in Double Porosity Transport

As has been previously stated, the Chalk is considered to be a dual porosity aquifer with a large volume of effectively immobile pore water and a highly mobile but relatively small proportion of water in the fracture component. Using typical parameter values Barker (1993) estimates flow rates of a few mm/day in the fissure component and just 1mm per year in the matrix under the same head conditions. Since the small pore-throats and associated strong capillary forces inhibit movement of water in the matrix porosity, the main transport process in the matrix is molecular diffusion. This is also a slow process and has been estimated as between 6 months and

5 years for diffusion over a 10cm matrix block (Barker, 1993).

The recognition of the significance of matrix diffusion in influencing solute transport in the Chalk is well known and a number of studies (e.g. Bibby, 1981; Black and Kipp, 1983; Barker, 1985) have examined examples and proposed models for the migration and diffusion of solutes in dual porosity Chalk. The behaviour of a contaminant in a double porosity system is related to the contact time between fracture and matrix water and the extent to which molecular diffusive exchange can interact and cause concentration changes in that time with diffusive exchange becoming more significant at longer times (e.g. Foster and Crease, 1975; Downing et al., 1979; Wellings, 1981; Barker, 1986; Mathias et al., 2005).

In the context of bromate, identifying the extent to which the bromate solute has diffused into the matrix blocks and the relative concentration of bromate in matrix and fracture water is critical in order to establish the migration of the bromate contaminant in the matrix system. In addition to uncertainty regarding the history and magnitude of bromate release (see Fitzpatrick (2010)), little pore water data are available and all monitored bromate concentrations reflect those of pumped or bailed groundwater arising from the fissure system. Although this thesis can make predictions as to the extent of porewater contamination, no quantitative data are available to validate such predictions and increases uncertainty on future predictions.

Barker (1993) and Ward et al. (1998) define four characteristic styles of transport in which the significance of dual porosity diffusive exchange varies. These have been characterised in terms of relative proportions of three characteristic times; the time for advection (t_a), the time for diffusion across a matrix block t_{cb} (as a function of the block size and solute diffusion coefficient) and t_{cf}, the time for diffusive equilibrium to be achieved between a fracture and matrix porewater, is related to the surface area of the fracture.

- If the advection time (t_a) is relatively short with respect to the diffusion times, matrix diffusive exchange is negligible and the aquifer can be characterised as an effectively single porosity media by the fracture porosity and groundwater flow velocity. Case studies of this type of diffusive exchange are relatively rare except in laboratory settings (Barker, 1993)

- If the advection time is a small fraction of that for diffusion across a matrix block (i.e. $t_a, t_{cf} \ll t_{cb}$) diffusion from the fracture can still affect contaminant transport depending upon the surface area available for diffusion (a function of fissure aperture and length), the properties and geometry of the matrix blocks can be ignored since they have negligible effect. Well-developed large aperture fractures such as those enhanced by dissolution tend to result in this form of transport (e.g. Atkinson and Ingle Smith, 1974; Mathias et al., 2006).

- If the advection time is similar to that for diffusion across a matrix block

($t_a, t_{cf} \approx t_{cb}$) the diffusive exchange with the matrix attenuates transport and the shape and size of matrix blocks is critical in influencing the form and magnitude of contaminant breakthrough. Long duration contamination occurrences such as those described by Lawrence and Foster (1991); Lawrence et al. (1996) and Watson (2004) are examples of this style of transport.

- If the advection time is long relative to the block diffusion time ($t_a >> t_{cb}$) then matrix diffusive exchange dominates transport and the Chalk will behave as a single porosity aquifer dominated by the properties of the matrix and the properties of the fracture system (which by inference must be poorly developed). An example of such a system is diffusion-dominated solute transport influencing porewater concentrations in deeply buried Chalk (Edmunds et al., 2001).

The key physical parameters for considering dual porosity transport in the Chalk are therefore those which directly influence the relative size and shape of the fracture and matrix blocks as a function of fracture spacing, aperture, and geometry. Barker (1985) defined an empirical Block Geometry Function (BGF) to characterise these parameter for blocks of certain idealised shapes (e.g. spheres or parallel slabs). It has been shown in this chapter that many of these properties (i.e. fracture aperture, morphology, matrix porosity) are related to the bulk structure and stratigraphy of the Chalk aquifer. If data can be established for a section of aquifer, then dual porosity transport can be modelled using empirically determined parameters (for example from tracer tests) for the fracture system, following the approach taken by Watson (2004).

3.8 Conceptual Hydrostratigraphy of the Hertfordshire Chalk

The aim of this chapter has been to establish the physical properties of the Hertfordshire Chalk Aquifer in terms of its stratigraphic and structural framework in order to determine the likely influence upon the transport of bromate. From this review a conceptual hydrostratigraphy of the aquifer is presented against which the additional complexity imposed by the karst flow system of Hertfordshire can be considered.

- The Chalk Group forms the major aquifer of the region, however, the Grey Chalk group is not considered to be a contributory unit to flow or bromate transport in Hertfordshire. The Plenus Marls at the Base of the Holywell Nodular Chalk probably mark the base of the effective aquifer and may be a locally confining unit.

- The majority of groundwater flow occurs in the New Pit and Lewes Nodular Chalk formations of the White Chalk Group and these are the main contributory units in major public supply abstraction boreholes. Owing to the regional dip the significance of the New Pit Chalk diminishes eastward. The Seaford Chalk, the dominant Chalk formation encountered at outcrop only contributes to the aquifer in the east of the region in the vicinity of the Lee Valley. Newhaven Chalk may be locally preserved in the core of a synform in the vicinity of Hoddesdon.

- The Chalk Rock Member of the Lewes Nodular Chalk Formation is potentially a highly important regional flow and transport horizon, being relatively shallow in the vicinity of the bromate source at Sandridge, and possessing low primary porosity due to mineralisation, and relatively wide, clean fractures due to its hardness. These characteristics may limit the extent to which double porosity diffusive exchange can attenuate bromate transport.

- The Melbourn Rock may also be a major flow horizon, although since it occurs only at depths typically > 60m, the extent to which fissures are transmissive and or transporting bromate is unknown.

- The regional piezometry reflects the overall structure of the Chalk following the dip slope in a broadly south-easterly direction. The North Mymms Recharge Mound appears to be related to structural features, probably a combination of normal faults and anticlinal doming. Groundwater levels show a strong seasonal trend in the Chiltern Hills however this becomes increasingly damped in an eastward direction reflecting increased transmissivity. The overall spatial distribution of groundwater elevations is relatively constant

- Literature derived transmissivity and storage data are highly variable for the region, and is further complicated by construction of adits and localised hydraulic enhancement at major abstraction wells, however, the data do appear to be consistent with the overall range for the UK Chalk aquifer.

- Primary porosity and fracture spacing and aperture appear to decrease with depth and stratigraphic level, however little if any site specific data are available to better characterise the aquifer in Hertfordshire.

- Normal fault development between North Mymms and Hatfield may contribute to an apparent steepening of hydraulic gradients in this area.

- The regional geomorphology and surface drainage pattern also appears to reflect the major structural and stratigraphic trends formed of a combination of NW-SE fracture set, a secondary NE-SW set and a tertiary N-S set that might be linked to the occurrence of normal faults.

- The nature of the weathered interface between overlying units and the Chalk aquifer in Hertfordshire is is poorly described and uncertain across much of the area. However, the degree of weathering of particular interest at two locations; close to the bromate source zone and at the interface with the fluvio-glacial deposits within the Vale of St Albans.

- The Upper Glacial Gravels form a perched aquifer but are not considered to be involved in bromate transport. The Anglian Boulder Clay (Lowestoft Till) may locally confine the Chalk and underlying Kesgrave Gravels in the Vale of St Albans. The Chalk and Kesgrave Gravels are likely to be in hydraulic continuity where present.

- No pore water data exist other than for the Bromate Source zone and it is not possible to estimate the significance or spatial variation in double porosity diffusive exchange, this will limit the confidence in any predictive transport models.

The conceptual understanding described above is illustrated vertically in Figure 3.14 and spatially in Figure 3.15.

It is recognised that this characterisation is relatively general since available field data for the Hertfordshire Chalk aquifer are relatively sparse and the possibility that local variations may occur is likely. In the absence of site specific data, tentative dual porosity modelling parameters for the Chalk formations of the Hertfordshire Chalk aquifer based upon the literature data and stratigraphic characterisation, are presented in Table 3.9. This approach is not intended to be robust since at the present time it cannot be validated against field data, however it should give a broad indicative estimate of the relative significance of dual porosity diffusive exchange in each aquifer unit.

Unit thicknesses are relatively well constrained by geophysical measurements (Woods, 2003, 2006; Randle, 2005). Fracture spacings have been based upon that described in accordance with BS 5930 1999 as in Mortimore (e.g. 1993); Jones and Robins (e.g. 1999) or inferred from physical measurements (e.g. Younger and Elliot, 1995; Bloomfield, 1996). Porosity data have been inferred from Price (1987); Matthews and Clayton (1993); Bloomfield et al. (1995). Fracture apertures are highly uncertain and are important parameters influencing transport. Limited data described in Section 3.4 has been used to estimate a possible aperture range. For conjugate fracture sets the sphere Block Geometry Function of Barker (1985) may be appropriate whilst for orthogonal fractures such as those of the Seaford Chalk the parallel slab geometry is more appropriate.

The properties of Lewes Nodular Chalk are much more variable due to frequent hard grounds and nodular horizons with generally widely spaced ($0.6-2$m) conjugate joint sets and hence the sphere BGF of (Barker, 1985) may be appropriate.

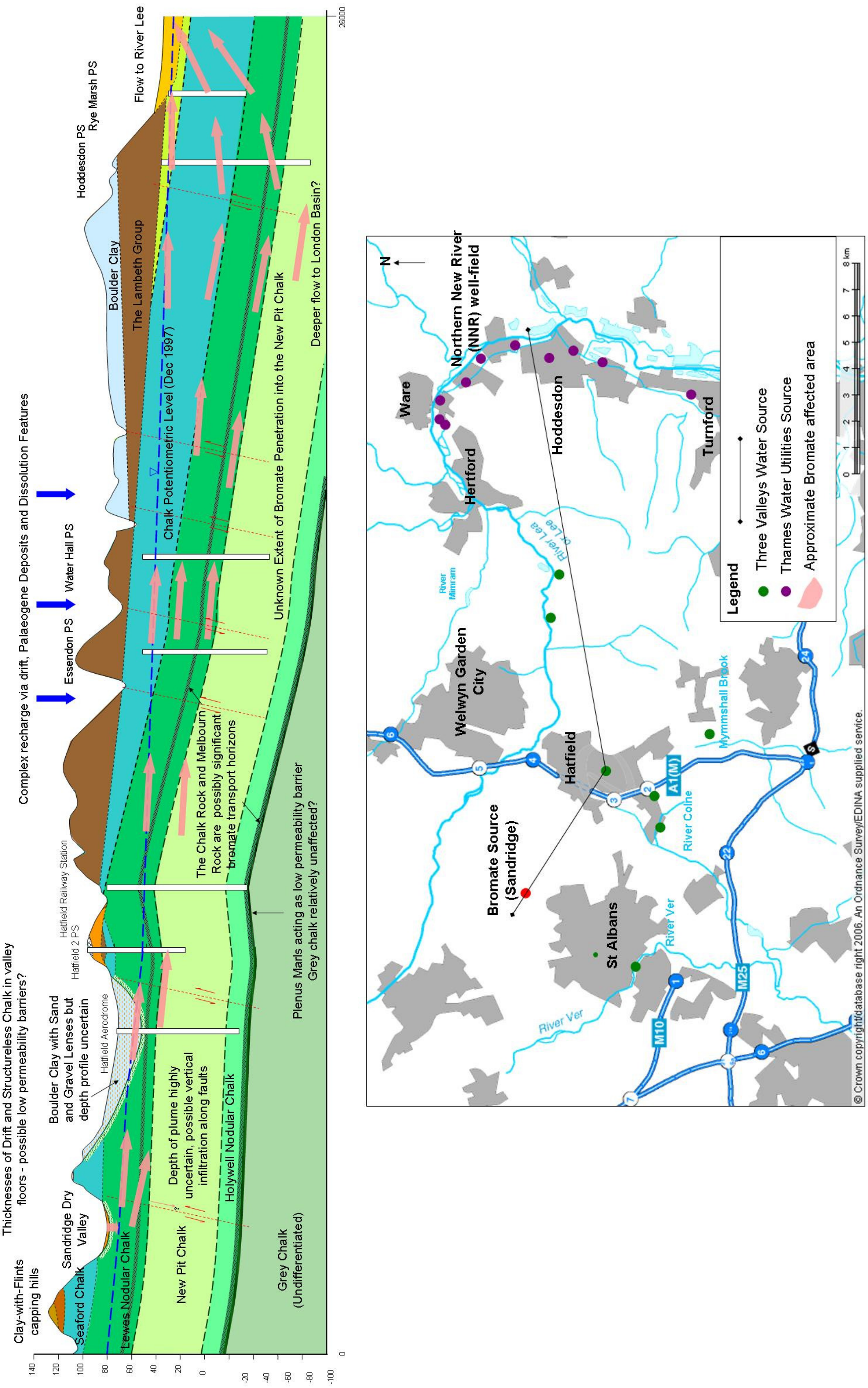


Figure 3.14: Conceptual Understanding of the hydrostratigraphic function of the Hertfordshire Chalk Aquifer (Cross Section)

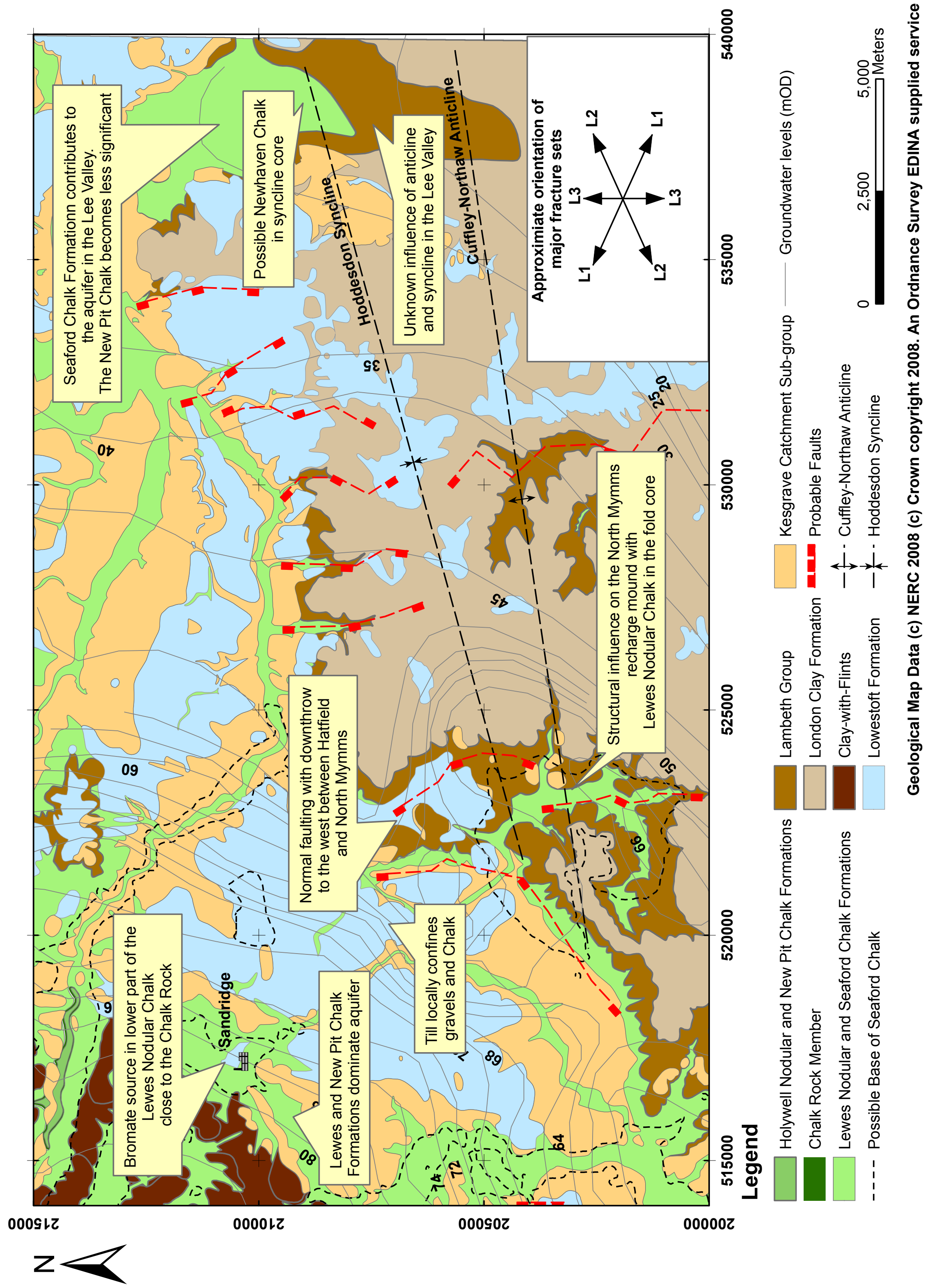


Figure 3.15: Conceptual Understanding of the hydrostratigraphic function of the Hertfordshire Chalk Aquifer (Spatial)

The Chalk Rock due to its unusually low primary porosity and high fracture aperture, should be considered a separate aquifer unit with widely spaced ($0.6 - 2$m) high aperture conjugate fractures. The sphere block geometry function of (Barker, 1985) may be appropriate.

The New Pit Chalk is a soft high porosity Chalk with frequent marls and rare flints. Fractures are typically conjugate and medium spaced ($0.2 - 0.6$m) but possibly are less well developed than the Lewes Nodular Chalk due to the depth of burial.

The Holywell Nodular Chalk is a hard low porosity shelly chalk with occasional marls and rare flints. Fractures are typically widely to very widely spaced (> 2m) and conjugate but probably poorly developed due to depth of burial.

The Melbourn Rock is a very hard low porosity hardground band with medium spaced ($0.6 - 2$m) conjugate fracture sets (Jones and Robins, 1999) possibly of wide aperture although the extent to which burial compaction has closed fractures is uncertain.

Table 3.9: Tentative estimated double porosity model parameters for the Hertfordshire Chalk Aquifer

Formation	Thickness			Fracture Spacing (m)			Aperture (mm)	Porosity (%)			Fracture Style
	Typical	Max	Min	Typical	Max	Min		Typical	Max	Min	
Seaford	50	55	45	0.4	0.6	0.2	0.5	38	50	20	Orthogonal
Lewes Nodular	37	40	34	1	2	0.6	0.1	37	45	20	Conjugate
Chalk Rock	5	10	2	2	6	1	0.1	10	15	5	Conjugate
New Pit	58	63	55	2	6	1	0.1	36	44	32	Conjugate
Holywell Nodular	17	18	16	4	10	2	0.01	29	44	20	Conjugate
Melbourne Rock	3	5	1	0.4	0.6	0.2	1	20	27	10	Conjugate

Chapter 4

The Development of Karst in the Hertfordshire Chalk Aquifer

4.1 The Origin and Characteristics of Chalk Karst

Calcite, the dominant mineral component of the Chalk, is prone to dissolution where it comes into contact with water bearing some acidity, and which is under-saturated with respect to calcium carbonate. Calcite dissolution occurs by reaction in the system between carbon dioxide (CO_2), water (H_2O) and calcite ($CaCO_3$) and is summarised by equation 4.1

$$CaCO_3 + CO_2(g) + H_2O(aq) \rightleftharpoons Ca^{2+} + 2HCO_3^- \tag{4.1}$$

The presence of CO_2, either in the soil or dissolved from the atmosphere enhances calcite dissolution by generating additional acidity in the aqueous solution, the amount of CO_2 entering solution being dependent upon the temperature, air pressure and biogenic processes (Kaufmann, 2003), in addition a proportion of the dissolved CO_2 can become hydrated to form carbonic acid (H_2CO_3) (equation4.2).

$$CO_2(g)atm \rightleftharpoons CO_2(aq) + H_2O(aq) \rightleftharpoons H_2CO_3(aq) \tag{4.2}$$

Subsequently the carbonic acid can disassociate leading to a further increase in acidity.

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \tag{4.3}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \tag{4.4}$$

As calcite dissolution progresses, ${CO_3}^{2-}$ association with H^+ increases the alkalinity and thereby buffers the dissolution reaction leading to a reduction in reaction rate as carbonate system begins to equilibrate. Given the buffering capacity of the

Chalk, this implies that recharge must have an important role in the formation of dissolution features.

The equilibrium between P_{CO_2} in solution and calcite is non-linear and close to equilibrium the solution rate decreases by several orders of magnitude. Equilibrium is rarely achieved where there is active flow and the groundwater will tend be slightly under saturated with respect to $CaCO_3$ (Worthington, 2003) further enhancing the potential for dissolution at locations where flow occurs rather than at stagnant zones.

The mixing of solutions with differing $HCO_3{}^-$ concentrations, which is a linear process as opposed to the non-linear carbonate equilibria, can lead to release of additional CO_2 which in turn leads to further acidity generation and enhanced dissolution. This process, termed mixing corrosion, was described by Bogli (1964, 1980, in Ford and Williams (2007)) and can occur between waters with different saturation with respect to P_{CO_2} and where $CaCO_3$ is $\leq$ 250mg/l. Mixing of this type is thought to commonly occur at discharge zones where water of differing origin and acidity is mixed (e.g. at springs), and may be important in the formation of karstic spring discharge points in the chalk (Price et al., 1993).

The dissolution of calcite can also be enhanced where water passes through an acidic cover deposit which can act to locally focus flow and increase its acidity, most commonly where oxidation of pyrite can occur by the reaction of Equation 4.5. Acidity enhancement may also occur due to organic humic acids in solution.

$$2FeS_2 + \frac{15}{2}O_2 + 5H_2O \rightarrow 4SO_4^{2-} + 2FeOOH + 8H^+ \tag{4.5}$$

For the UK Chalk, these additional acidity-generating conditions are most prevalent at, or close to, the feather edge boundary of the overlying Palaeocene deposits of the Lambeth Group which are rich in pyrite and organic material. Similar conditions occur around the flanks of areas of drift such as Clay-with-flints and it has also been suggested that such features might occur near the edge of Boulder Clay deposits (Banks, 1996). Acidity enhancement is most common where the overlying deposits are thin (typically $<$ 10m) (Matthews et al., 2000) possibly because of increased oxygen content and recharge flux.

Whilst dissolution can occur anywhere where infiltrating water comes into contact with the rock, of particular relevance in Hertfordshire is the presence of overlying units that locally focus infiltration and also lead to an increase in aggressiveness of the water. Units of this type, including the Lambeth Group, London Clay, Boulder Clay and Clay-with-Flints all occur within the bromate-affected area (see chapter 3).

4.1.1 Spatial Development of Chalk Karst

Conditions suitable for downward percolation of water into the Chalk through overlying deposits have existed since the initial sub aerial exposure of the Chalk during the late Palaeocene (Jones, 1981; Edmonds, 2001*b*). As calcite solubility increases with the atmospheric pressure of carbon dioxide and at lower temperatures, the formation of dissolution features may have occurred at much faster rates in the past due to cooler glacial and periglacial conditions (Lord et al., 2002). Permafrost development would probably have restricted the depth of downward groundwater percolation and acted as an impermeable boundary layer focusing flow and therefore dissolution laterally above and below the zone of permafrost (e.g. Younger, 1989; Lloyd and Hiscock, 1990).

However, the rate of dissolution can be dependent on a combination of factors including rainfall, topography and climate, it remains uncertain whether chalk dissolution might be more prevalent under hot or cold climates (Matthews et al., 2000) and to what extent it is occurring under present conditions.

Several studies (e.g. Culshaw and Waltham, 1987; Matthews et al., 2000; Edmonds, 2001*a*, 2008) have attempted to characterise the occurrence of chalk dissolution features and the environmental and geological characteristics that are favourable to their formation. Most of these studies come from a geotechnical perspective and relate primarily to the likely locations of subsidence hazards caused by dissolution pipes and sinkholes and do not necessarily reflect the likely locations of hydrogeologically important features. Although not precisely defined the following generalisations can be made:

- Chalk dissolution features appear to be concentrated at the feather edges and junctions of overlying units and also beneath such units

- Dissolution features are also common along former and present surface water drainage paths, dry valley floors and to some extent valley side slopes. They are also more common in the upper parts of dry valleys (Lord et al., 2002)

- Occurrences of dissolution features are also closely related to the course of the Proto-Thames and glaciated regions of Hertfordshire (Edmonds, 2001*b*)

- Sometimes dissolution features are clustered at the crest of Chalk escarpments (e.g. Warren and Mortimore, 2003) possibly due to plateau run-off associated with impermeable Clay-with-Flints

- In the Chalk aquifer, dissolution is often focused at zones of water table fluctuation both past and present. Conduits also tend to develop close to the base level of the system, i.e. the elevation of the draining springs, and will tend to follow a tortuous path just above and below this elevation (White, 2003)

- Dissolution feature occurrence is also influenced by lithological characteristics of the underlying chalk and may be more prevalent in high porosity formations such as the Seaford and Culver Chalks (Mortimore et al., 1990). Stronger, low porosity chalks which posses a denser grain packing may be more resistant to dissolution. Such variations might arise either from lithological controls (such as coccolith species variations or occurrence of hardgrounds) and/or the depth of burial, diagenesis and tectonic compaction

- Dissolution feature occurrence is less frequent in the Grey Chalk due to an increased marl and reduced carbonate component (Lord et al., 2002)

- Dissolution has also been observed to be influenced by the heterogeneous stratigraphy of the chalk and may preferentially develop at horizons along which flow is either confined or directed by relatively impermeable or poorly fractured features such as persistent marls and flint bands and hence may extend sub-horizontally along bedding (Warren and Mortimore, 2003)

- Structural features such as fold hinges, fault zones and zones of stress relief fracturing also contribute to increased occurrence of dissolution features, especially if they act to open fractures and increase infiltration and flow. Many karst flow systems tend to develop sub-parallel to fold axes (e.g. White, 1993; Vesper et al., 2001; Perrin and Luetscher, 2008) particularly in synclines which act to both focus flow and increase occurrence and aperture of fractures.

Maurice et al. (2006) suggest a conceptual model for the evolution of karst within the chalk aquifer of Berkshire, UK. This is based on a simple principal of Palaeocene escarpment retreat and solution lowering of the chalk surface (Figure 4.1) which can be classified into three geomorphological zones based upon the distribution and hydrogeological significance of the karst features.

- Zone 1 comprises the area where chalk is overlain by Paleogene deposits locally dissected by rivers and streams to expose chalk in the valley floors. Most dissolution features are present and may be actively forming in this zone associated with runoff from the Palaeocene contact and as well as sub-surface conduits feeding springs.

- In Zone 2, stream sinks are generally absent and recharge is dominantly diffuse onto the dip slope of the Chalk. Solution lowering of the Chalk surface has left residual deposits of Clay-with-Flints along with associated dolines which may focus drainage. There may also be relict conduits at depth which have not been removed by solution lowering or erosion. Surface waters are fed by ephemeral bournes which may have a contribution from karst conduits.

- In Zone 3 Superficial deposits and surface karst features are generally absent or have been entirely eroded. Recharge is likely to be diffuse across the outcrop with dry valleys being the dominant surface drainage feature.

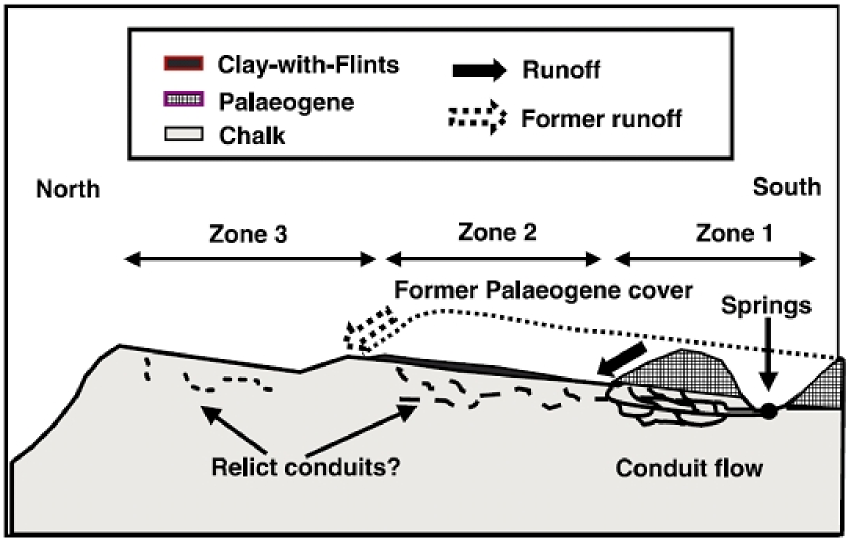


Figure 4.1: Conceptual model of chalk conduit formation based on geomorphological features, as the Palaeocene escarpment retreats and the chalk on the dip slope is weathered and eroded conduits become inactivated, removed or infilled, reducing groundwater flow velocities and increasing attenuation of any transported solutes (Maurice et al., 2006)

4.1.2 The Morphology of Chalk Karst and dissolution features

Although the Chalk landscape is not a true karstic terrain where the geomorphological forms are dominated by dissolution, the chalk outcrop does exhibit many geomorphological and hydrological features indicative of karst development including but not limited to dry valleys, blind valleys, subsidence features and dolines, swallow holes and ephemeral springs. The formation of discrete surface karst is associated with valley floors suggesting a close relationship to run-off and it is likely that dissolution affected chalk of varying age might exist at differing elevations across a catchment due to the ongoing evolution of surface drainage paths.

On a broad scale, diffuse recharge of the Chalk by rainwater (where acidity is provided by dissolved CO_2) has lead to widespread solution lowering of the entire chalk land surface and also has contributed to the formation of capping layers of Clay-with-Flints (*ss*) (Jukes-Browne, 1906*a*; Catt and Hodgson, 1976) derived from the insoluble residue of the solution weathering. Studies of preserved stratigraphy in Clay-with-Flints deposits in the French Chalk have indicated up to 200m of Chalk might have been removed by this method (Laignel et al., 1999)

Where chalk recharge occurs in the presence of overlying units, it rarely occurs in a diffuse manner. Topography and geomorphological processes channel run-off into valleys and rivers and also focus infiltration through fingering along more permeable flow paths. This process focuses runoff and recharge leading to areas of preferential dissolution. The resulting contact between overlying formations and the Chalk can be highly irregular and typically takes a castellated form pinnacled by the non

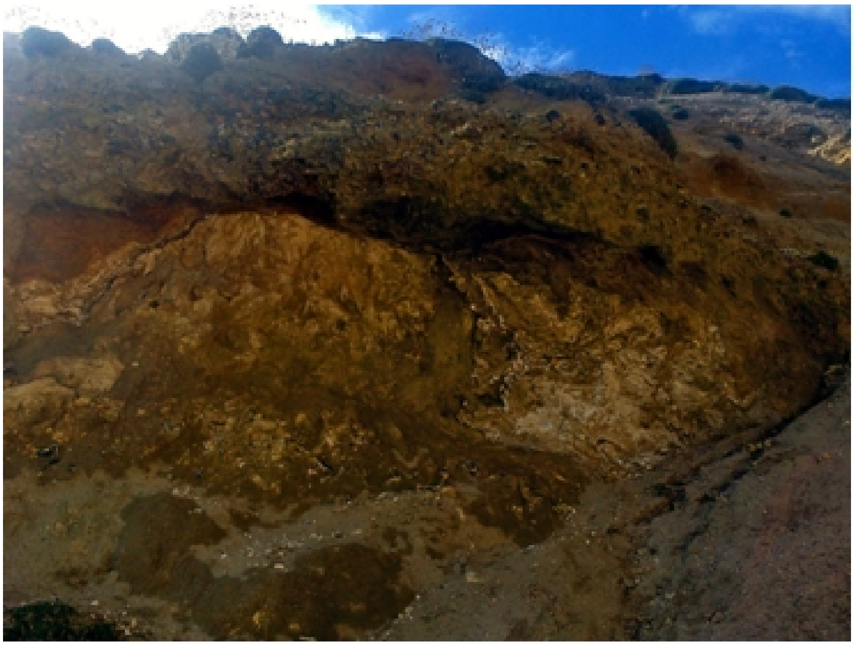


Figure 4.2: In-situ solution lowering, alteration and cryoturbation at the Palaeocene/Chalk interface, Castle Hill, Newhaven Sussex

uniform solution lowering. This is typified in observations of cliff top exposures on the Sussex coast and has also been observed in engineering cuttings and trial trenches (e.g. Warren and Mortimore, 2003) and is illustrated in Figure 4.2

Chalk dissolution can be highly variable in form and are often gradational between characteristic types from discrete solution enlarged fractures to conduits, pipes and even large caves, this variability is illustrated in figure 4.3

Dolines, are generally defined as a topographic feature associated with solution related closed depressions. As a result, the term doline only relates to the surface expression of dissolution and does not imply a mode of origin. Dolines can form from the collapse or subsidence sinkholes or swallow holes or through general discrete solution lowering of the land surface. They can occur both within the chalk outcrop or on foundered overlying material and can vary in size from less than a metre to 10s of metres in diameter.

Not all dissolution features produce a surface expression, some may occur with little or no disturbance to the overlying cover. This is most common where cover deposits can be rearranged at depth by subsidence (for example loose sands running into voids) or in cohesive soils where the cover deposit may bridge the dissolution void. In most cases the limited surface disturbance is temporary and voids can migrate rapidly upwards when destabilised, for example by inflow of water (Edmonds, 2001*b*), and thus may rapidly develop a surface expression as a subsidence or collapse sinkhole (Figure 4.4). Collapse sinkholes are relatively rare in the chalk, however a high density of such features has been observed in some localised areas (e.g. Edmonds, 2001*a*; McDowell et al., 2008).

Dissolution sinkholes are the results of focused dissolution on the chalk surface

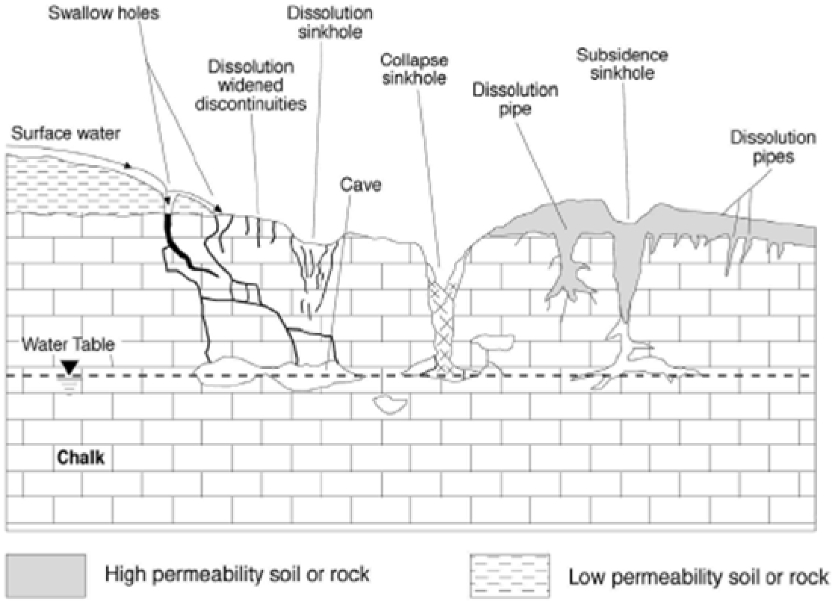


Figure 4.3: Morphology of typical Chalk karst features (Lord et al., 2002)

where it is not overlain by superficial deposits resulting in enlargement of fractures surrounding causing the matrix blocks to gradually collapse together.

Dissolution pipes are the most frequently encountered discrete dissolution feature in the Chalk (Lamont-Black and Mortimore, 2000). These features are typically in the form of partially or completely infilled pipes and can vary in diameter from a few cm up to 30m in diameter (Lord et al., 2002). The profile is typically cylindrical or elliptical and diameter generally reduces with depth due to the buffering of the acidity by the carbonate dissolution process. Despite this limitation, some deep (up to 80mbgl) clay filled dissolution pipe and chimney karst features have been observed in tunnels in the Lewes Nodular Chalk and Holywell Nodular Chalk in Kent (Warren and Mortimore, 2003) associated with deep solution beneath and adjacent to Clay-with-Flints deposits. Dissolution pipes may also extend laterally along discontinuities or lithological features typically in the form of radial branches from the central pipe (Figure 4.5).

Swallow holes (e.g. Figure 4.6) are of the particular hydrological significance, as the name suggests, these are sinkhole features that “swallow”a surface water stream and provide a direct connection between surface water and groundwater systems. Swallow holes act as both the downstream terminus of surface water catchment and the upstream headwaters of conduit systems (White, 1993). Swallow holes in the chalk most commonly occur close to the boundary of impermeable cover units where stream runoff is directed onto the chalk and begins to infiltrate the fracture system and dissolve the bedrock and often develop in groups along the length of a water course. Subsidence sinkholes that open up beneath a stream can often develop into stable swallow holes. As the feature develops it may eventually attain sufficient drainage capacity to absorb the entire stream input.

Figure 4.4: Collapse/Subsidence Sinkhole acting as a swallow hole in Palaeocene Lambeth Group, Hatfield House, Hertfordshire. Tape measure is 1m for scale

Figure 4.5: Typical solution pipe morphology with sheet pipe lateral extension downward along joints and lithological discontinuities, Culver Chalk, East Sussex

Figure 4.6: Swallow hole, Water End, Hertfordshire

Solution enlargement of fractures to form the "secondary fissure" component of Price (1987) are the most important chalk karst feature in terms of the effect on aquifer properties. This morphology of the dissolution is variable from development of channels in the fracture surface to a more diffuse enlargement of the entire feature (Price et al., 2000) and can lead to high fracture transmissivity as aperture increases. The hydrological feedback induced by such heterogeneity in the transmissivity can often become self-organising leading to development of dendritic conduit networks (Worthington and Ford, 2009) as flow lines are focused towards and along conduit features leading to further dissolution and enlargement.

"Master conduits" or fractures might develop that have a effect upon the regional flow regime and may carry a large proportion of the flow, despite being of relatively small overall size. This is particularly the case in areas where flows might already be concentrated such as at discharge points and along valley axes (Price et al., 1993). Surveys of subsurface fractures in adits suggests that enhancement of the system by dissolution appears to be operate on a discrete basis rather than universally and actively flowing enlarged fractures are spaced on the order of several metres to several tens of metres apart based on measurements from adit systems (Price, 1987; MacDonald et al., 1998).

The solution-enhanced fracture systems may take the form of a single discrete conduit/fracture or a number of tortuous conduits which may intersect and result in highly anisotropic flow regimes. Solution enlargement of fractures and development of master conduits is often thought to be closely related to the position of the water table and sheet like dissolution features can develop within zones of water table fluctuation (both past and present). As with other characteristics relevant to the chalk aquifer properties such as porosity and fracture style karst development has in cases been also correlated with stratigraphy such as hardgrounds, sheet and semi-tabular flint bands and along marl seams.

Fractures may also become enhanced where groundwater mixing occurs by corrosion mixing, for example at the intersection of two fractures bearing differing water compositions or at the junction of a fracture carrying diffuse recharge water with that of a conduit carrying recent allogenic recharge. The act of mechanical mixing may lead to release of carbon dioxide and a subsequent increase in calcite solubility. This can lead to development of anisotropy depending upon the relative flows in the two systems.

A further form dissolution feature are dissolution tubules (Lamont-Black and Mortimore, 2000). These features are associated with lithological discontinuities such as sheet flints, marls, hardgrounds, major fractures and caves. They form bifurcating voids extending upward from the discontinuities for a distance between 50 and 3000mm and can be laterally extensive over at least several hundred metres. They are considered to form in the seasonally unsaturated zone due to interactions between recharge and the water table. They may form transmissive and laterally persistent horizons within the zone of past and present water table fluctuations.

Solution enlargement of fractures may be related to the formation of dissolution conduits although these are morphologically distinct features. Maurice et al. (2006) define chalk karstic conduits as tubular features between 10mm and 1000mm in diameter and between several metres to several kilometres in length.

Larger scale development of dissolution may lead to formation of a cave system, although such systems are rare in the chalk. In engineering literature (e.g. Matthews et al., 2000; Lord et al., 2002) this is thought to be because the relatively weak shear strength of the chalk limits the size of stable caverns in the sub-surface. Recorded examples of caves in the UK are generally restricted to coastal areas such as at Peacehaven and Beachy Head in Sussex (Mortimore and Pomerol, 1997) which are associated with preferential dissolution along a fault and tabular flint seam respectively. Cave systems are also known inland such as at Blackheath (Lord et al., 2002). Caves tend to be more common in the French Chalk where karst features are better developed (e.g Lacroix et al., 2002; Rodet et al., 2006).

4.1.3 Properties of the Karstic Chalk Aquifer

The terminology used to describe karst development in the chalk aquifer is loosely constrained and often interchangeable between authors; secondary fissures, fractures, channels, conduits have all been used to describe both similar and also very different features in terms of their origin and influence. Up to this point the terminology used has been that as described in the literature, however to avoid ambiguity the remainder of this thesis adopts a simplified terminology:

- Fractures shall refer to approximately 2 dimensional planar features dominantly of tectonic or stress related origin (e.g. joints) however, the term shall

(a) 15cm diameter conduit on marl band

(b) 4cm diameter conduits on harground

(c) 2cm diameter solution enlarged fracture

Figure 4.7: Borehole televiewer images of conduits and solution enlarged fractures in the Berkshire Chalk (Maurice, 2008)

also be used to describe solution enhanced fractures since in a carbonate aquifer it is probably difficult and indeed may be inappropriate to distinguish purely tectonic fractures from those enhanced by dissolution.

- "Conduits" shall refer to approximately circular or tubular features, including channels in fissure surfaces or caves, which primarily originate from dissolution of the chalk matrix.

Karst development in the subsurface acts to concentrate groundwater flow within the solution enhanced porosity and locally increase the transmissivity of that porosity through increased aperture and velocity of groundwater flow. Historically there has been a spread of debate over whether the chalk could be considered a true karstic aquifer where nearly all flow is concentrated in the solution enhanced porosity (e.g. Worthington, 2003; White, 2003) to only possessing some karstic characteristics such as rapid flows (e.g. Banks et al., 1995; Maurice et al., 2006). Despite this, it is widely recognised that the solution enhancement of the aquifer contributes to the observed hydraulic properties and indeed may be necessary to explain the apparently high transmissivity as compared to that which might arise from the non solution enhanced fracture system only (e.g. see section 3.4 and Price (1987)). There has been further debate over whether it is appropriate to consider the karstic chalk aquifer as a dual porosity (matrix-fracture) system or if a triple porosity (matrix-fracture-conduit) (e.g. Worthington, 2003; Worthington and Ford, 2009) or double dual porosity (matrix-fracture and fracture-conduit) system (e.g. Price et al., 1993) might be a more appropriate. Whichever terminology is adopted, there is likely to be both a mechanical and diffusive exchange of water between the matrix, fracture and conduit porosities, which themselves a continuum of sizes. There is probably a shift in the significance of each system depending upon the problem in question.

Conduits are approximately circular features in cross section and exhibit different flow characteristics to those of a granular or fractured media. A conduit can be approximated by considering flow through a pipe, governed by Poiseuilles Law. The discharge through a pipe under these conditions is proportional to the pressure drop along the pipe, the radius of the pipe and inversely proportional to pipe length and fluid viscosity. Where flow occurs under laminar conditions, discharge through such a pipe is governed by the Hagen-Poiseuille equation (Equation 4.6).

$$Q = \frac{\pi d^4 \rho g}{128\mu} \cdot \frac{dh}{dl} \tag{4.6}$$

Where Q is discharge, d is the pipe diameter, dh is the drop in head, dl is the pipe length, ρ is the fluid density, g is acceleration due to gravity and μ is the fluid dynamic viscosity. Discharge is proportional to the fourth power of the tube diameter, and an ideal conduit will be much more transmissive than an ideal fissure of similar aperture. This proportionality contributes to the positive feedback influencing the development of master conduits. In karst systems, it may be inappropriate to assume laminar flow since as the conduit increases in size sinuosity and roughness the likelihood of turbulent flow eddies developing increase. Turbulent flow in a pipe can be calculated using the Darcy-Weishbach equation (Equation 4.7).

$$Q = \left(\frac{2dga^2}{f}\right)^{1/2} \cdot \left(\frac{dh}{dl}\right)^{1/2} \tag{4.7}$$

Where Q is discharge, d is the pipe diameter, a is the conduit cross sectional area, dh is the drop in head, dl is the pipe length, g is the acceleration due to gravity and f is a friction factor dependent upon the roughness of the conduit walls and sinuosity. Friction factors are typically determined empirically and proportional to discharge. The development of a conduit and enlarged fracture system in the chalk aquifer imparts an additional degree of heterogeneity and anisotropy. Worthington (2003) suggests that conduits and enlarged fractures dominate flows but result from a minimal increase in overall porosity compared to the fracture system alone (Table 4.1).

Table 4.1:]
Properties of the Chalk matrix-fracture-conduit system in karstic Chalk (after Worthington, 2003)

Component	Porosity (%)	Hydraulic Conductivity (m/s)	Flow Volume (%)	Storage Volume (%)
Matrix	30	1×10^{-8}	0.02	99.9
Fractures	0.01	4×10^{-6}	6.0	< 0.1
Conduits	0.02	6×10^{-5}	94.0	< 0.1

MacDonald and Allen (2001) examined the relationship between transmissivity and distance from overlying Palaeocene deposits but were unable to identify a clear correlation. A possible explanation being that since conduits and enlarged fractures only constitute a relatively small percentage of the rock volume, the chance of directly intercepting such a feature in a well is very low (Worthington, 2003). Whilst dissolution may be enhanced and more active close to the Palaeocene, features may have developed prior to the recession and erosion of the Palaeocene to it's present outcrop (e.g. the model of Maurice et al. (2006)) and transmissivity development need not be directly related to the present outcrop.

Determining quantitative properties to characterise karstic chalk systems is challenging since accessible caves are relatively rare. The most readily available evidence for the inference of the existence of karst development within the chalk aquifer is that of tracer tests which indicate rapid flows, typically on the order of a few 100m a day to a few km a day (Harold, 1937; Atkinson and Ingle Smith, 1974; Price et al., 1992; Banks et al., 1995; Maurice et al., 2006) and can extend over a distance of several kilometeres. The velocities reported by such tests fall well within the range of that established as typical for tracer tests conducted in established karstic conduit dominated systems (Worthington, 1994) however, the approach of estimating the aperture using the cubic law (e.g. Atkinson and Ingle Smith, 1974; Price, 1987) and see section 3.7.2.1) suggests apertures in the range of only a few mm, and therefore a high degree of karst widening or conduit development does not necessarily need to be invoked to account for the rapidity of the flow.

4.2 The Occurrence of Surface Karst in Hertfordshire

Having established the conditions for the formation and style of karst development, this section describes the distribution, morphology and behavior of karst features developed within the bromate-affected area of Hertfordshire.

4.2.1 The Regional Hydrostratigraphy and the Context for Karst Development

The hydrostratigraphic framework established for Hertfordshire presented in chapter 3 provides the context for the development of karst. Of the conditions likely to be favourable for karst development as described in section 4.1.1, many apply to Hertfordshire and in combination lead to conditions highly favourable for karst development:

- Palaeocene deposits of the Reading Formation overly the chalk above a warped sub-Palaeocene feather edge in the southeast of the region. There is potential for acidic run-off across, through and beneath this contact. The relative elevation of the Palaeocene escarpment above the Chalk of the Vale of St Albans and the relatively impermeable London Clay which overlies the Reading Formation acts to direct additional surface run-off from the Palaeocene escarpment onto the Chalk.

- The former course of the "Proto-Thames" which has been correlated with a high density of dissolution features (Edmonds, 2001*b*), passes through the Vale of St Albans. This may have enhanced karst feature development adjacent to and beneath the valley and could be linked to former groundwater and surface water drainage which may not have been coincident with the present day arrangement.

- Clay-with-Flints development is intrinsically linked to that of solution lowering of the Chalk and there is increased potential for solution feature development adjacent to and beneath such deposits.

- Dissolution has been linked to stratigraphic formation and characteristics in the Chalk, the soft, high porosity Seaford Chalk Formation is particularly prone to solution. It was shown in section 3.2.1.2 that the Seaford chalk formation is likely to be the dominant formation present at outcrop. In the subsurface, both the Seaford Chalk Formation and Lewes Nodular Chalk formation contains vertical heterogeneity arising from marls, flints and hardgrounds at which groundwater flow could be concentrated and dissolution potential enhanced.

- The structural form of the aquifer can also influence the development of karst by controlling the occurrence and style of fractures, faults and other features such as folds which in turn influence the magnitude direction of groundwater flow. In Hertfordshire at least two major fold axes are developed across the Chalk-Palaeocene boundary in a WSW-ENE orientation sub-parallel to the direction of regional groundwater flow and have caused a thinning of the

Palaeocene near Cuffley. Normal faulting has also been inferred and linked to valleys in the Palaeocene and Chalk particularly in the area around Hatfield and could influence groundwater flow in this area.

4.2.2 Dolines, Sinkholes and Swallow Holes

The most obvious indication of karst is where dolines, subsidence sinkholes and swallow holes are visible at ground level. A number of previous studies of dissolution feature development in Hertfordshire have been conducted (Wooldridge and Kirkaldy, 1937; Kirkaldy, 1950; Walsh and Ockenden, 1982) and have particularly focused on the area around North Mymms and Hatfield. Additional survey work was conducted by the National Rivers Authority (Newton, 2005*a*) (now the Environment Agency) relating to the development of groundwater source protection zones in the 1980's.

A map of known dissolution features in the area (Figure 4.8) has been compiled from references in literature and those marked on Ordnance Survey mapping. Also indicated are the distribution of Palaeocene deposits and the water table (as at October 2000). The following trends relating to the occurrence of these features can be observed:

- Nearly all features occur less than 1km from the edge of the Palaeocene deposits except for those in the area of the Great Wood on the Cuffley brook and its tributaries, however the thickness of the Reading Formation thins in that area.

- Nearly all features are associated with present drainage courses and in particular the majority of swallow holes and Dolines occur in and adjacent to the Mymmshall Brook Valley and it's tributaries.

- Swallow Holes around Hatfield appear to be related to dry valleys and ephemeral drainage courses possibly suggesting that they may be older features associated with former drainage courses or have now been made redundant by head retreat of rivers and exposure of chalk higher up the catchment.

- The occurrence of solution features and drainage patterns in the Mymmshall Brook catchment appears to be related the periclinal dome in the Sub-Palaeocene surface identified by Wooldridge (1920), the eastward extent of this structure also appears to be associated with the Cuffley Brook/Great Wood features.

- The water table and North Mymms recharge mound also appears to be associated with the high density of swallow holes in the area which suggests that all three are related.

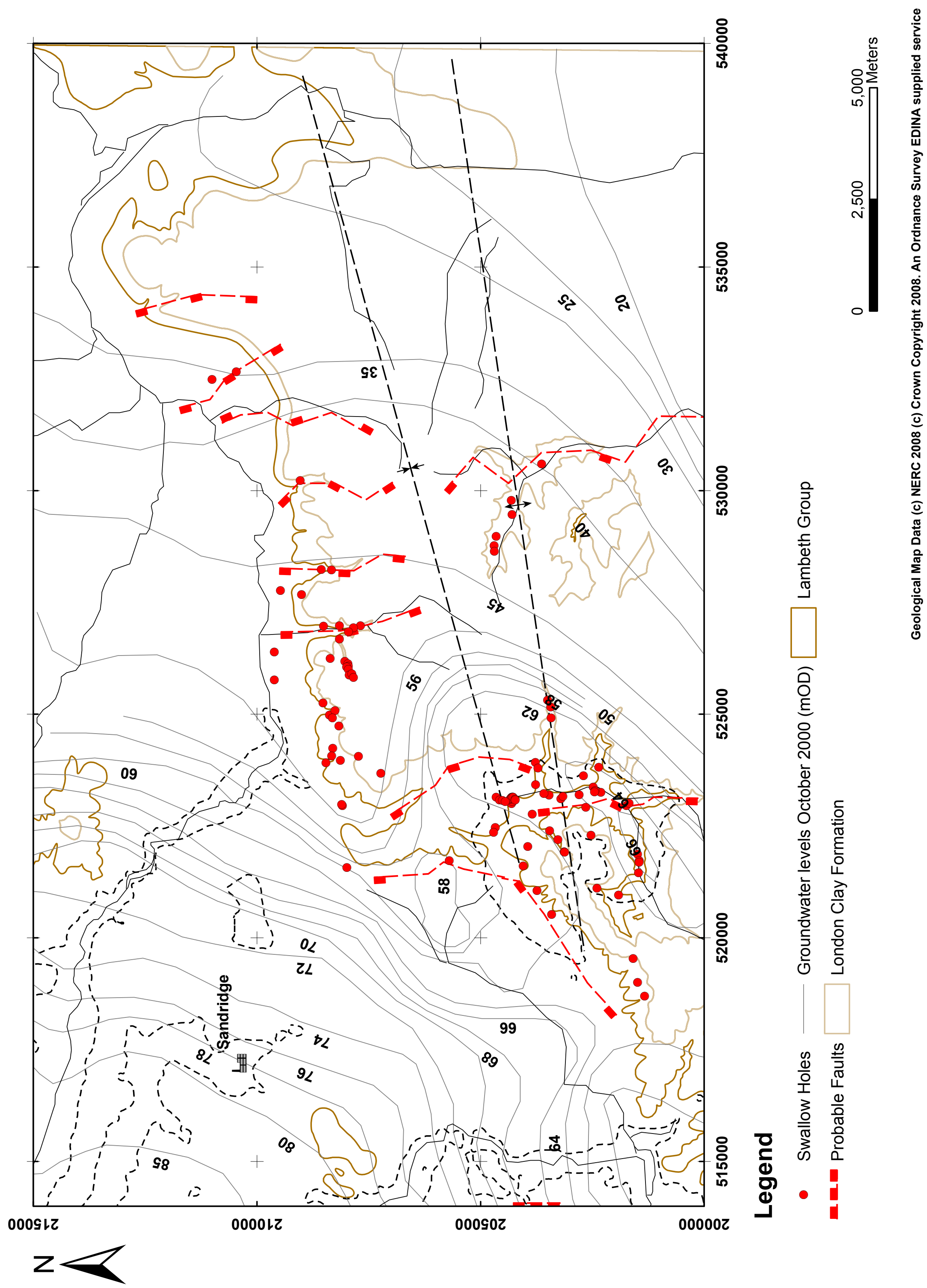


Figure 4.8: Map of chalk swallow holes between North Mymms and Hertford (Compiled From Kirkaldy, 1950; Walsh and Ockenden, 1982; Newton, 2005*a*; Bloomfield et al., 2004, and field observations)

There is likely to be bias in the mapped occurrences of solution features, such features being easier to detect where there is a surface expression and where they are intimately associated with drainage courses. Sub-surface dissolution features are only commonly detected during intrusive investigations, for example in engineering works and given the rural nature of the area the extent of such works is limited. There remains potential for undetected solution features to be present, particularly relict high level dissolution features away from present drainage courses.

4.2.2.1 The Water End Complex

The complex at Water End (NGR TL 231 043) is the best known example of chalk swallow hole development in the UK and has been investigated by a number of studies; (Whittaker, 1921; Wooldridge and Kirkaldy, 1937; Kirkaldy, 1950; Walsh and Ockenden, 1982; Waltham et al., 1997), the most comprehensive being that of Walsh and Ockenden (1982). The complex is positioned in a blind valley up to 10m deep (Waltham et al., 1997) within the Palaeocene outcrop and at the confluence of two drainage courses; the Mymmshall Brook and the Welham Green Bourne. It is likely that the positioning of the swallow holes and the stream confluence are related due to their respective influences on surface drainage patterns.

In its present state (Figure 4.9) the complex is rough and marshy with low scrub vegetation. The surface morphology has changed with time, ranging from apparently deep swallow hole craters with exposed fractured chalk in the 1930's (Kirkaldy, 1950) to hummocky scrub grassland to the present state which may reflect a continuation of the state in the early 1980's whereby vegetation was encouraged to provide a habitat for the rearing of game birds (Walsh and Ockenden, 1982). Chalk is no longer visible at the surface and the main depressions have either been infilled by sediment or overgrown. The form of the land surface is influenced by a combination of factors including climate, sediment load of the incoming streams, as well as farming and land management practice within the catchment. Sporadic subsidence and collapse events also appear to have changed the surface morphology with time (Kirkaldy, 1950; Walsh and Ockenden, 1982) and new sink and swallow hole development appears to follow flood events (Waltham et al., 1997).

The Water End Swallow Hole complex is approximately 400m^2 and contains at least 17 discrete swallow holes or dolines ranging from a few metres up to 12m in diameter. The dissolution features of the Water End complex appear to comprise two main types as described below and indicated in Walsh and Ockenden (1982).

- Funnel shaped holes with steep conical faces which are drained by discrete fissures

- Shallow soakaway basins where flow appears more diffuse through the sediment in the basin floor

(a) Dry Conditions

(b) Flood Conditions

(c) Recession Conditions

Figure 4.9: Typical form of the landscape at Water End with incised drainage channels, swallow holes and overgrown vegetation. Approximately the same view is shown during dry, flood and recession conditions

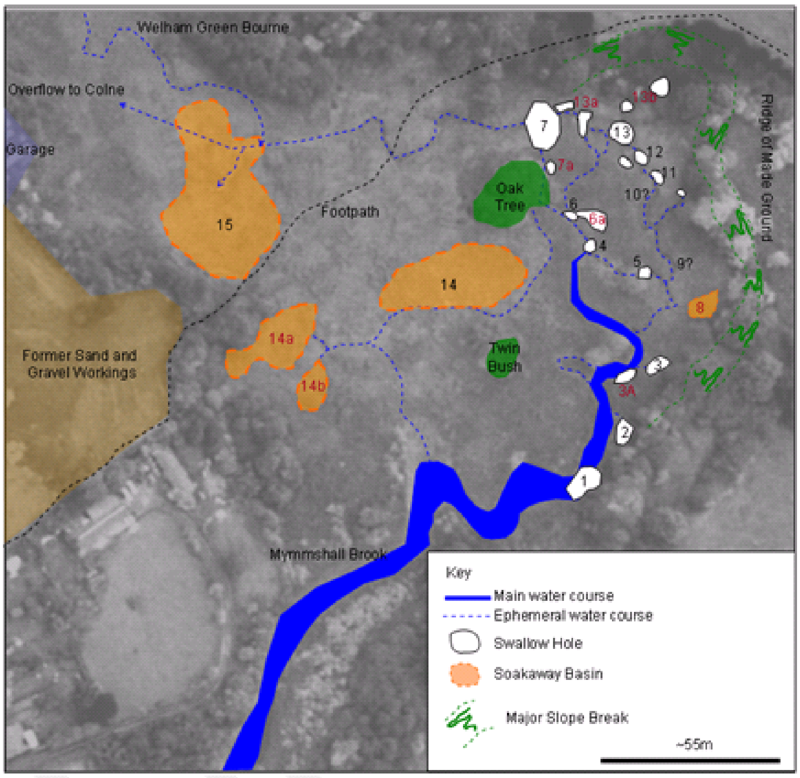


Figure 4.10: Map of the Water End Complex in 2007 showing main swallow holes and soakaway basin, where possible feature numbers from 1982 are consistently labelled

A recent remapping of the swallow hole distribution based upon aerial photograph interpretation and field visits undertaken in February 2007 (Figure 4.2.2.1) following a relatively dry preceding week and several changes can be noted from the 1982 study.

- A number of new swallow holes are present (3a, 6a, 7a, 13a); these appear to have opened close to existing features. Enlargement of existing features has also occurred at features 6 and 7.

- 2 collapse features are present in the northeast; there was no apparent evidence of connection to a drainage path (13b) and these may represent collapse over a void at depth

- Ephemeral drainage paths indicate minor changes in channel morphology and also a number of overflow connections to the Soakaway basins

- Changes to the channel morphology exist around features 8,9 and 10 and it was not possible to identify these features it is possible they may have become infilled, there is some evidence of soakage around the approximate location of feature 8.

- Standing water was present in Soakaway basin 15 with evidence that basins 14a, 14b and 14 had also been recently active due to soft bare ground.

Table 4.2: Shallow Geological Sequence at the Water End Swallow Hole Complex (after Walsh and Ockenden, 1982)

Max. Thickness Encountered (m)	Description	Probable Origin
2.25	Soft dark grey and black organic silt/clay	Recent Flood and alluvial deposits
2.45	Firm light brown slightly gravely silt/clay	Recent alluvial deposits
1.05	Firm greenish brown clay	Foundered Lambeth Group
0.45	Greenish brown and reddish brown sand	Foundered Lambeth Group
0.27	Firm brown silty clay with occasional chalk fragments	Possible insoluble residue of Chalk
0.45	Soft white chalk with flints	Cretaceous

- The flow of the Mymmshall brook appeared to continue as far as feature 4 or 6 although due to the extensive undergrowth and soft ground these could not be reached to confirm.

- Soft, wet ground and bare soil in the base of features 7, 13, 12 and 11 indicated recent activity.

The soakaway basins are approximately $3 - 3.6$m above the chalk surface according to Kirkaldy (1950) and a sedimentary sequence determined for the complex by Walsh and Ockenden (1982) is presented in Table 4.2. Recent deposits dominate being up to 5m thick across the complex, foundered Palaeocene deposits infill bowl shaped depressions in the chalk upper surface and are irregularly developed across the site. The Chalk is described as being "honeycombed" by caves and fissures which allow rapid drainage (Walsh and Ockenden, 1982). Caves of at least metre scale are inferred from a quote; "*down which a man might be carried*" of J.M Hopson (1892) Whittaker (in 1921).

The caves form narrow rifts with some solution enlargement and appear to lose water through fractures in their base (Walsh and Ockenden, 1982). These features have been followed for approximately 10-20m (Waltham et al., 1997). From their morphology these caves may have originated as near surface sub-vertical fractures that have been widened in a combination of stress release and dissolution.

The Water End swallow holes operate in a processional fashion from the entrance point of the Mymmshall Brook at the south of the complex. Increasing run-off leads to occupation of swallow holes further into the complex and if run-off continues to increase a lake forms ponding over the entire complex (see figure 4.9). Whittaker (1921) speculated that the lake represented localised rising of the water table to the ground surface under conditions of high recharge, however, the water level in at the North Mymms PS approximately 500m south of the complex remains relatively constant at approximately 12m below ground surface even following heavy rain (Walsh and Ockenden, 1982) and flooding of the complex is probably due to choking of the swallow holes by debris or by the volume of infiltration exceeding the capacity of the complex which is estimated to be approximately $1\text{m}^3\text{s}^{-1}$ (Walsh and Ockenden, 1982).

When the infiltration capacity of the swallow hole complex begins to be exceeded, the Mymmshall Brook begins to overflow to the northwest along a channel which forms the headwater of the River Colne. Overflow into the Colne is related to peak run-off and discharge into the Water End complex from the Mymmshall Brook and the Welham Green Bourne but is strongly dependent upon preceding conditions (Atkins, 2006). Bypass flow to the Colne occurred between 0 and 56 days a year in the period 1927-1936 (Harold, 1937). This is comparable to more recent measurement of 12 days per annum (Walsh and Ockenden, 1982) and contemporary measurements recorded flow in the Colne on 38 days out of 142 (Atkins, 2006) (equivalent to 98 days per annum pro-rata), although these data were collected in winter and early spring so correspond to the wettest period of the year. It is likely that in summer months the frequency of bypass flows is reduced and the annual proportion of bypass flows might be closer to that of 1927 - 1936. The overflow channel to the Colne also contains swallow holes; Wooldridge and Kirkaldy (1937) reports that an attempt to build a canal along the channel was halted because swallow holes developed in the banks prevented adequate water retention.

4.2.2.2 The Mymmshall Brook Catchment

The Water End swallow hole complex is positioned at the at the lowest point of Mymmshall Brook stream catchment which drains an area of approximately $45 - 50\text{km}^2$ south of the bromate-affected area. The majority of the catchment is underlain by London Clay which prevents infiltration and surface run-off dominates and only a relatively small proportion of the catchment is developed within the Lambeth Group and Chalk. Run-off is likely to be highly acidic due to the sub-soil chemistry and the flow of acidic water directed into the Mymmshall Brook in combination with the favourable geological setting have contributed to the high density of dissolution features in the valley.

Estimates of flow in the stream are highly variable, ranging between $108 - 45,000\text{m}^3/day$ with a the total annual flow in the stream estimated of order of $3,000,000\text{m}^3$/year (Walsh and Ockenden, 1982). Recent flow gauging indicated maximum flows of up to $474,000\text{m}^3$/day and a mean daily flow of $10,600\text{m}^3$/day (Atkins, 2006). Spot gauging upstream of Water End by the Environment Agency $2005a$ and Atkins (2006) recorded flows in the range $2160 - 180,921\text{m}^3$/day.

The Mymmshall Brook contributes 80% to 90% of the flow entering the Water End swallow hole complex (Atkins, 2006) the remainder is provided from the Welham Green Bourne which enters from the North East and includes the Potterells Swallow Holes within its catchment. Owing to its smaller catchment, flows from the Welham

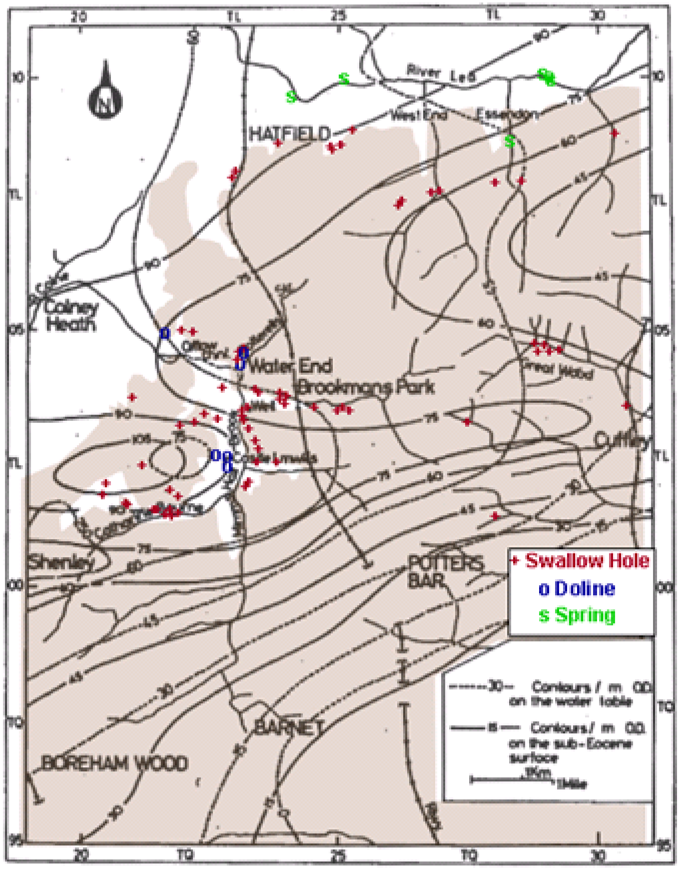


Figure 4.11: Compilation Map of Swallow Hole Locations in the Mymmshall Brook Catchment from fieldwork and literature (Kirkaldy, 1950; Walsh and Ockenden, 1982; Bloomfield et al., 2004)

Greene Bourne often peak prior to that of the Mymmshall brook and the exact relative contributions vary following rainfall events.

A number of swallow holes are present adjacent to, and within the stream bed and flow is lost along the entire course where it overlies the chalk (Whittaker, 1921). In particular, swallow holes are reported in the reach close to Mymms Hall (approx NGR TL233020) and Whittaker (1921); Kirkaldy (1950) provide approximate locations of at least five swallow holes in this area. Another set occur approximately 500m northeast of Mymms Hall (Whittaker, 1921). Other features are either offset from the main stream course or visible as circular depressions and appear to be dominantly associated with bends in the course of the river. The distribution of dissolution features within the catchment is presented in Figure 4.11.

Other minor swallow hole clusters are developed within the Mymmshall Brook catchment and are described below:

- In the region of Gobions Wood (Approx NGR TL252034), close to the Palaeocene boundary and developed within a tributary valley to the Mym
- 3 small hollows about 250m North East of Warrengate Farm (NGR TL 239 023). A further three are noted just to the south of these by the stream Whittaker (1921).

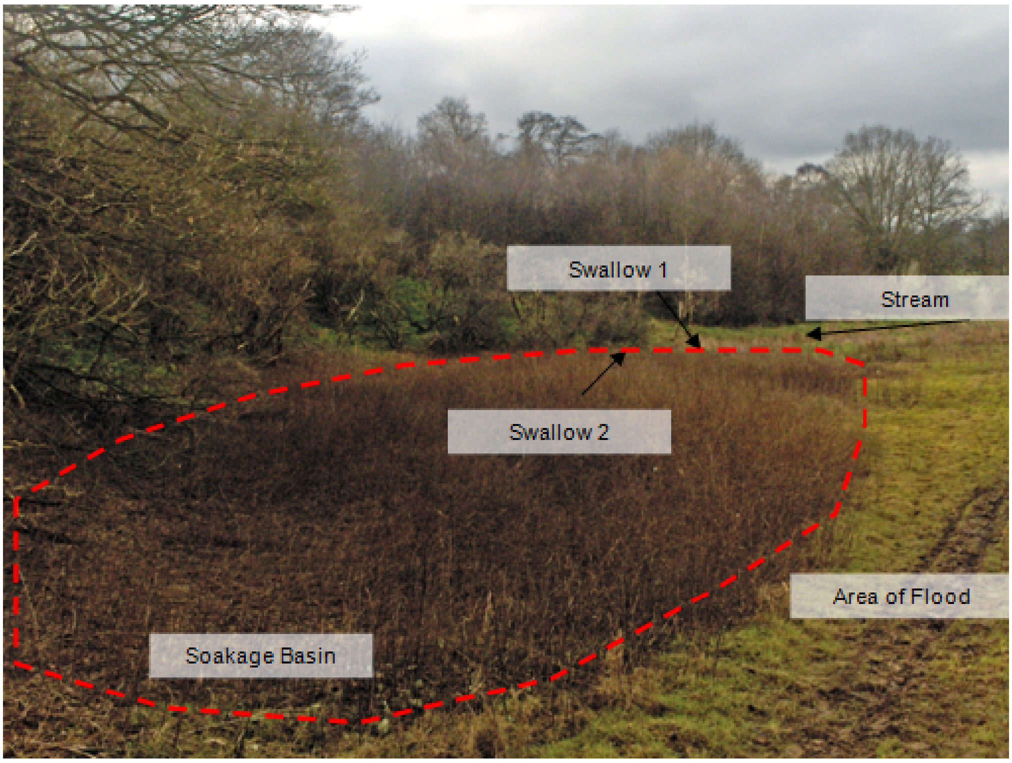
- 3 Dolines form circular depressions just west and south west of Castle Lime Quarry (Kirkaldy, 1950).

- The Catherine Bourne Swallow hole (Figure 4.12(b)), approximate NGR TL214014) occurs as part of a small complex of Dolines and Swallow Holes occurring adjacent to the Catherine Bourne Stream, a tributary to the Mymmshall Brook. The main Swallow Hole forms a conical depression approximately 6m deep and $15 - 20$m in diameter. It is offset by approximately 20m from the stream course and is fed by a small incised channel on its southern side. This swallow Hole is overgrown with bushes and scrub vegetation. Bypass flows of the Catherine Bourne swallow hole appear to be more complex than those at Water End and have been related to a variety of factors including preceding flow, depth of water in the swallow hole, channel morphology and vegetation (Atkins, 2006). The maximum recorded flow in the Catherine Bourne entering the swallow hole has been measured to be at least $0.023\text{m}^3/\text{s}$ (Atkins, 2006). Flow in the Catherine Bourne might be influenced by abstractions at North Mymms PWS, with flows bypassing the swallow hole being rare since operation of the well and only occurring during "abnormal weather" (Lee Conservancy Board, 1935). The swallow holes in the Catherine Bourne may be within the well catchment zone and possibly have a highly transmissive connection to the well that is acting as a rapid drain of sub-surface water.

- Swallow Holes and Dolines occur in the area of Hawkeshead Wood on the western Flank of the Mymmshall Brook Valley. They are relatively close to the Castle Lime Quarry and are possibly related to drainage from the Palaeocene capped topographic high.

- At Potwells (NGR TL 219 031), approximately 100 downstream of a confluence of three streams draining high ground underlain by London Clay and situated in Reading Formation at an elevation above the level of the Mymmshall Brook. A hummocky area of approximately 25m by 15m contained at least 2 circular swallow holes up to 1.5m in diameter and dead bracken and grass indicated recent flooding over a soakaway basin (Figure 4.12(a)).

- On the Welham Green Bourne, an elongated depression approximately 450m by 50m in the region of the Potterells (NGR TL 234 047) is considered to be the result of a large number of subsidence collapses and solution lowering over swallow holes (Wooldridge and Kirkaldy, 1937). A number of discrete swallow holes and dolines also occur just north east of the Water End Complex.



(a) The Potwells swallow hole complex

(b) The Catherine Bourne swallow hole

Figure 4.12: Examples of other Swallow Holes developed within the Mymmshall Brook Catchment

4.2.2.3 Castle Lime Works Quarry

An exposure of dissolution features at Castle Lime Works Quarry (approx NGR TL229025) has been partially preserved as a Geological Site of Special Scientific Interest (SSSI). The quarry sited on the western flank of the Mymmshall Brook valley and is approximately 10m above the level of the Mymmshall Brook and approximately 20m above the present water table. A wide variety of dissolution features have been encountered and since removed by workings of the quarry (Waltham et al., 1997), however from the literature, it is possible to compile a summary of the key types of karst features present.

The exposed chalk is overlain by a less than a metre of reddish clay and flints (Waltham et al., 1997). This possibly represents a thin layer of solution-derived Clay-with-Flints. The chalk upper surface appears to be pinnacled and contains shallow basins or dolines up to 3m deep and 30m wide infilled with Bullhead Bed Palaeocene gravels and sands with clay partings. The chalk itself is described as soft flinty chalk and is of the *Micraster coranguinum* Zone (Wooldridge and Kirkaldy, 1937) approximately equivalent to the modern Seaford Chalk Formation.

The quarry face shows discreet sheet pipes of sub-horizontal solution-enlarged fractures infilled with sands and clay extending laterally. The largest vertical pipe is approximately 10m in diameter in the former pit base (Kirkaldy, 1950) however this has been backfilled and is no longer exposed. The pipes appear to be related to mainly vertical joints that have been enlarged to produce dissolution pipes.

Also present are sub horizontal sheet pipes occurring between 6-15m below natural ground level. These features are laterally persistent varying in length from a few metres to around 50m and vary in thickness up to a maximum of approximately 0.9m. Despite bedding features and flint bands being obvious heterogeneities the sheet pipes do not appear related to flints or marls and have instead been linked to previous level of the water table (Kirkaldy, 1950).

The deepest observed features occur approximately 18m below the Palaeocene contact, where the Chalk shows intricate randomly oriented veining and seams of chocolate coloured clay with some yellow sand between 3 and 25mm thick (Kirkaldy, 1950). The solution pipes (both vertical and horizontal) are infilled with a chocolate coloured clay matrix supporting rinded and un-rinded, occasionally glauconite stained flint cobbles suggesting foundered Lambeth group and Clay-with-Flints. The clay matrix also contains chalk fragments of fine gravel up to cobble size. The contact at edge of the solution pipes is dominantly a clean boundary of sometimes slickensided black clay, a common indicator of Clay-with-Flints related dissolution (Catt and Hodgson, 1976). Occasionally on the upper surface of the sheet pipes are intricate veins penetrating up to 1m from the main feature, initially these appear tubular then branch and penetrate further along discontinuities (Kirkaldy, 1950). This description appears similar to that of branching dissolution tubules as described by Lamont-Black and Mortimore (2000) and the positioning above sheet pipes implies a similar mode of origin.

It is likely that most features in Hertfordshire are infilled with material derived from foundered Palaeocene deposits of the Lambeth group, probably representing that of the Reading formation as has been determined at Castle Lime Quarry (Waltham et al., 1997). However, it is possible that some features might also be associated with the Clay-with-Flints hill top plateaus in the north west of the region and close to Sandridge. Drift has been observed infilling the core of dissolution features, within an outer surround of foundered Reading Formation at Castle Lime Quarry (Wooldridge, 1920).

4.2.2.4 Other Swallow Hole clusters

Other Locations at which swallow holes occur in Hertfordshire are as follows:

- At Howe Dell (approx NGR TL229079) in the South of Hatfield a cone shaped depression up to 6m deep absorbs a northward draining ephemeral stream into several swallow holes at its base. As with Water End, flooding has been reported following heavy rain in 1875 and 1885. This resulted in the swallow holes being excavated, stabilised and cleared to a depth of around 6m below ground level to increase the rate of unimpeded drainage (Whittaker, 1921).

- A number of swallow holes are present in the vicinity of Hatfield House lake (NGR TL240084) close to the Chalk-Palaeocene boundary. Anecdotal evidence suggests these have been known since construction of the lake in the 16th century and new collapse features form regularly in the winter (pers. comm. 2007).

- Hatfield Park grounds contain a number of swallow hole clusters (Appendix A) associated with small valleys draining the London Clay and Palaeocene escarpment. The largest complex occurs at Brickkiln wood (NGR TL248083) but also around the Lake, at Coombe Wood (NGR TL241076) and near to Conduit Wood (NGR TL247082).

- Deeve Wood contains a complex of swallow holes known as "Popes Pondholes". These are developed along the course of a small stream draining into the Essendon Brook and following a field visit in February 2007 showed evidence of ponding and recent activity.

- Swallow holes and dolines are also developed along the main course of the Essendon Brook in the vicinity of Backhouse Wood (NGR TL271084) and near to Little Berkhamstead in Bedwell park (NGR TL283083).

- A number of Swallow holes are also reported in the area of the Great Wood adjacent and in particular where tributary surface streams drain off the relatively steep Palaeocene slopes into the Cuffley Brook. This area is on the crest of the Cuffley-Northaw anticline and represents a location where the Palaeocene cover is thinned.

4.2.2.5 Other Possible Karst Features

Construction Logs of public supply boreholes for the Northern New River (NNR) provided by Robinson and Buckle (2004) suggest some evidence for the occurrence of deep solution enlarged fractures and dissolution features in the proximity of the Lee Valley.

- Red sand-filled fissures were observed at approximately 118mbgl in the Grey Chalk at Broadmeads PWS (NGR TL353139). This occurrence appears to be superficially similar to deep ($>$ 70mbgl) sand-filled fractures in wells described as dissolution features elsewhere in Southern England (MacDonald et al., 1998) and indicates the possibility of deep dissolution features and fractures throughout the whole of the Chalk stratigraphy in the area of the Northern New River.

- A "slight spring" inflow at approximately 70mbgl and probably within the New Pit Chalk at Broadmeads PWS. This is possibly associated with a stratigraphic feature, most likely relating to a marl seam or persistent flint band.

- A large ($\approx$ 2m) sub-vertical fracture is indicated between 173mbl and 175mbgl on the Turnford (NGR TL360044) log possibly indicating a solution enlarged fracture.

Worthington (2003) describes other features that are diagnostic of karstic development in a carbonate aquifer:

- Homogeneous aquifers tend to show symmetrical cones of depression around pumping wells; the heterogeneity of conduit and karst development tends to distort the cone of depression along the axis of a conduit.

- Troughs in the water table can develop around conduits due to the large difference in transmissivity between the conduit and the surrounding aquifer and such troughs often terminate at springs.

- Hydraulic gradients in karst aquifers tend to decrease in a down gradient direction, especially along troughs in the water table as described above due to increased transmissivity towards discharge locations such as springs. In homogeneous porous media an increase in hydraulic gradient is normally required to drive flow toward a spring.

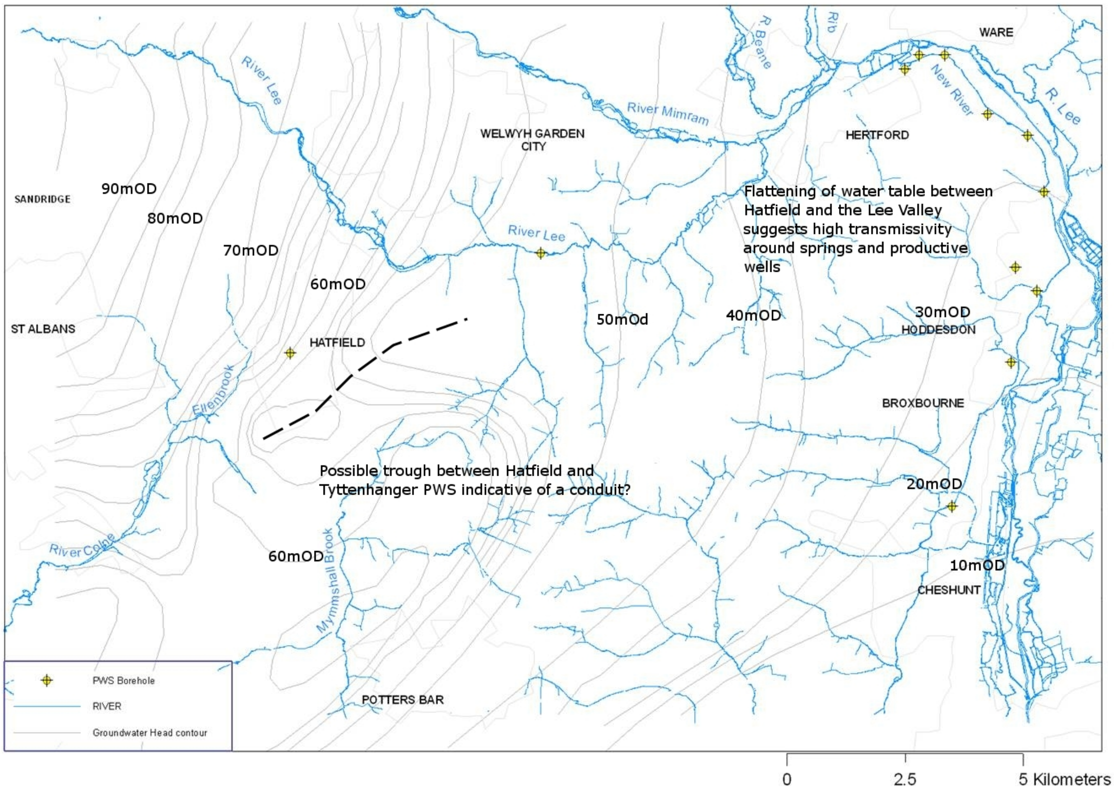


Figure 4.13: Evidence of conduit development from the regional piezometry. The general flattening of hydraulic gradients between Hatfield and discharge points in the Lee Valley is suggestive of high transmissivity, whilst the apparent trough/draw down between Hatfield and Tyttenhanger PWS and Roestock PWS is suggestive of possible conduit development and is coincident with the regional fracture fabric and the position of the Palaeocene feather edge.

Taking these diagnostic characteristics and examining the general form of the groundwater contours (see section 3.6) it is apparent that on a catchment scale there is an overall decrease in hydraulic gradient towards the Lee Valley in the east and that this is associated with the development of springs (see section 4.3) and very productive wells of the NNR well field. Conduit development may be further influencing the form of the water table in the causing the trough developed in an approximate NE-SW alignment between Hatfield and Tyttenhanger PWS and Roestock PWS (Figure 4.13).

4.3 Spring Discharges

Springs are common in chalk terrain, typically they are ephemeral bournes usually related to dip slope drainage and seasonal water table fluctuations. In karstic areas, springs represent natural output points of the conduit system and tend to be indicative of the base level of conduit development (White, 1993). The high transmissivity of karst aquifers results in low hydraulic gradients, and allows distributary flow paths and conduits to develop to more than one spring and at different elevations, the discharge from each spring being controlled by aquifer and conduit

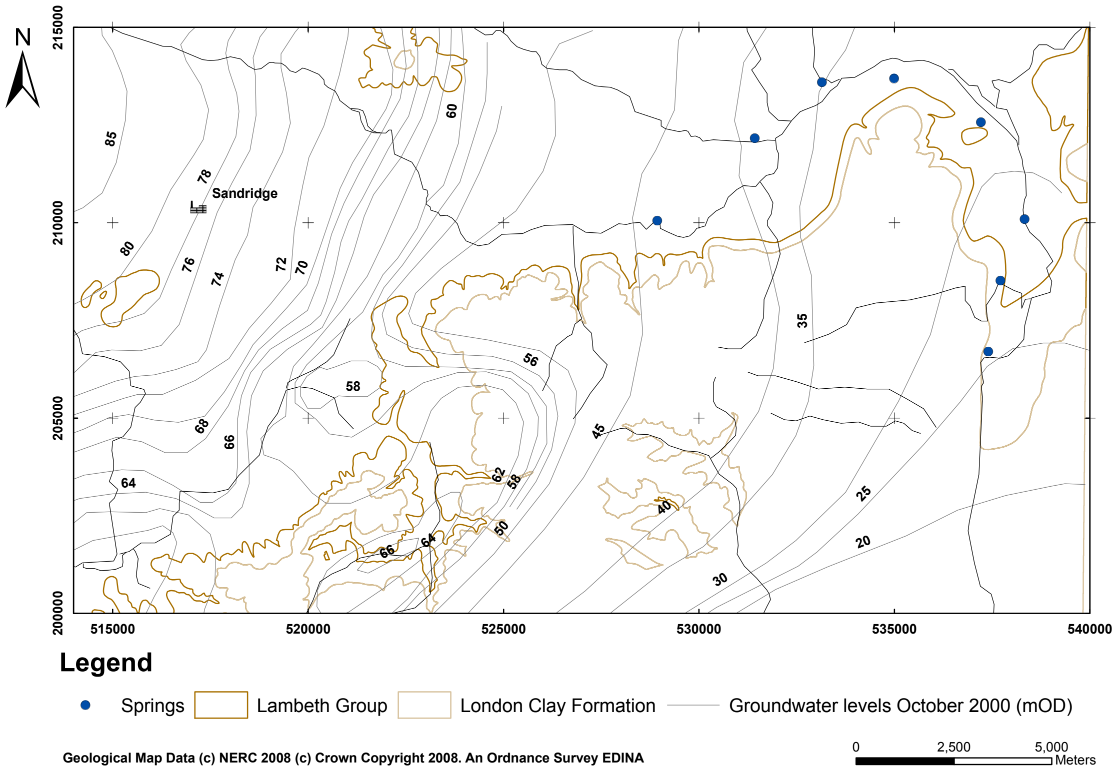


Figure 4.14: Regional Distribution of Spring Discharges (after Whittaker, 1921; Bloomfield et al., 2004). Piezometric contours are from (Buckle, 2005)

water levels. Springs occur where the conduit system either intersects the land surface or where flow is driven upwards, for example by an impermeable barrier. The distribution of major springs in the bromate-affected area is presented in Figure 4.14.

The highest set of springs in the area are occur at Whethampstead to the north of St Albans (NGR TL148149) and probably represent contact springs associated with the outcrop of the Chalk Rock. Similar springs also occur at Brocket Park (NGR TL221129) and Lemsford (NGR TL223123). Closer to the Palaeocene boundary the springs exhibit behaviour more characteristic of karstic fed springs and more importantly are natural outlet points for bromate-contaminated water.

4.3.1 The Woolmer's Park Springs

Arkley Hole spring and adjacent minor springs occur in a small wooded area known as Spring Wood (approximate NGR TL289101) in the grounds of Woolmer's park. A geological cross section (figure 4.15 of the spring and surrounding topography determined from BGS and OS mapping suggests that the springs occur above and within alluvial and glacial gravels on edge of the Lowestoft Till outcrop. The spring may be fed by a karstic fractures and conduits being within a few hundred metres of the Palaeocene outcrop and at an elevation less than 20m below the Paleocene boundary.

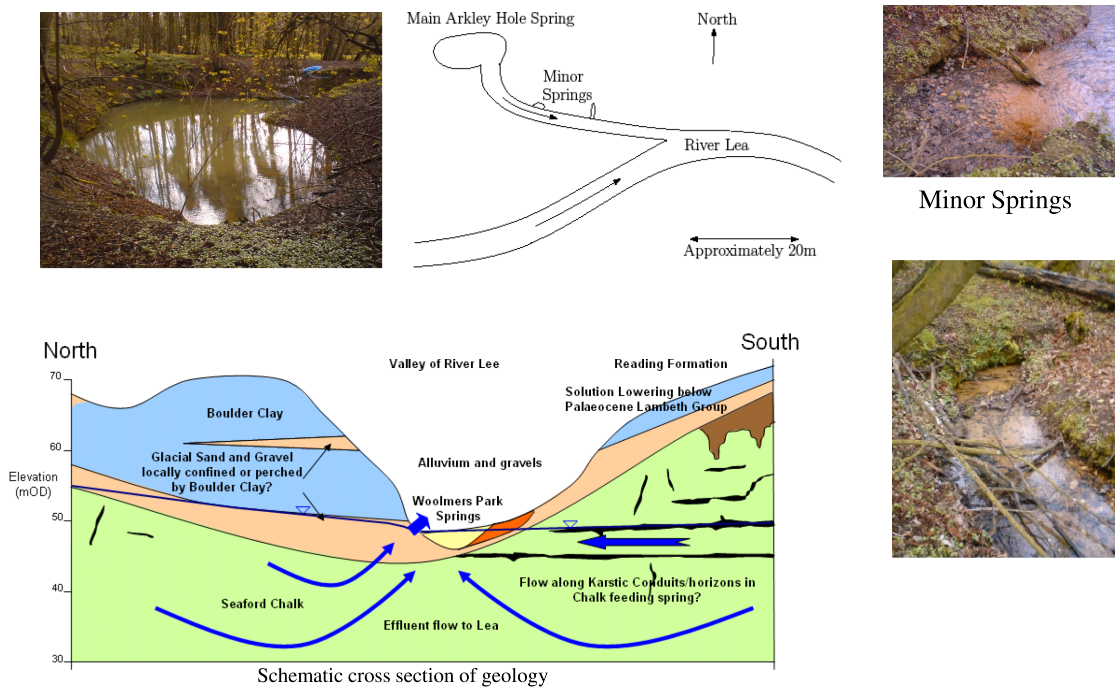


Figure 4.15: Map and schematic cross section of springs at Woolmer's Park. The geology has been derived from (BGS, 1978) and topographic data from Ordnance Survey (1999)

Arkley Hole spring rises in a elliptical basin approximately 10m by 5m and is connected to the River Lee by a 1-2m wide run-off channel. Several upwellings are visible and suggest a number of productive fractures or conduits converge at the spring pool. Spot gauging of discharge from Arkley hole indicates flows in the range $0.10 - 0.160\text{m}^3/\text{s}$ (Atkins, 2006). Two smaller springs/seeps are located approximately 30m south east of Arkley Hole and one has been gauged to show a flow of approximately $0.0037\text{m}^3/\text{s}$ (Whittaker, 1921). The flow regime is variable with periods of low discharge occurring occasionally allowing the spring pool to become stagnant and at times, the flow reversing, with the spring acting as a swallow hole to water from the River Lee. These changes probably reflect relative differences in the local river level, water table or different levels of flow (and drawdown due to abstraction) within the conduit system.

Arkley Hole spring responds rapidly to rainfall events and spring stream stage appears to rise and fall in accordance with that close to the Catherine Bourne and Water End swallow hole complexes, which suggests a similar response to rainfall events even if it does not confirm a direct connection to the swallow holes (Atkins, 2006). A stage discharge relationship for Arkley Hole has not been determined due to a lack of reliable data, the spring stage being affected by water levels of the River Lea during high flow periods.

4.3.2 Lea Valley Springs

A number of springs in the Chalk but also within the alluvial gravels exist along the entire course of the Lee Valley, a detailed qualitative account of theses springs is provided by Whittaker (1921).

The highest spring below the Mimram confluence is Chadwell Spring (Approximate NGR TL350136). The spring basin is approximately 27m in diameter and up to 5m deep and contains several "well defined fissures" (Whittaker, 1921) probably solution enhanced in the centre of the pool although recent field visits could not identify any obvious upwellings or inflow locations. Chadwell Spring was historically the main source to the New River and was thought to contribute up to 20000m^3/day (Whittaker, 1921) which is consistent with summary data collated by the Metropolitan Water Board between 1906 and 1969 (Newton, 2005*a*) although this probably reflects a peak flow since the average daily flow for the data is approximately 5000m3/day. As with Arkley hole, behaviour of Chadwell Spring is variable and has been observed to act as a swallow hole during conditions of low flow. Chadwell Spring is also affected by pumping from the nearby wells at Broadmeads PWS and Amwell End PWS (Whittaker, 1921).

Emma's Well spring (Approximate NGR TL372125) is situated close to Amwell Marsh and Amwell Hill pumping stations. Discharge at Emma's Well is inconsistent, apparent behaviour indicates long periods with no discharge interspersed with sporadic high discharges (Whittaker, 1921). It is probably strongly affected by nearby abstractions and the fracture/conduit network feeding the spring may be connected to, or intersect the network feeding Amwell Hill and Amwell Marsh abstraction wells which are both within a few hundred metres of the spring site. Further south, a number of small springs also contribute to flow in the New River between Amwell and Rye House yielding up to 36000m^3/day (Whittaker, 1921).

Between Hoddesdon and Broxbourne springs apparently show little temporal variation and yield around 27000m^3/day in summer (Whittaker, 1921). It is possible that these springs may be buffered with the gravels acting as store of water below the Lee and maintain discharges in the summer although pumping at Rye Common and Hoddesdon PS does appear to affect some southern Lea Valley springs according to Whittaker (1921) possibly referring to the Lynchmill and Rye House Springs. Lynchmill Spring is the largest in the area with two distinct outlets that have been incorporated into an ornamental garden (figure 4.16).

Water Cress beds near Broxbourne are mentioned as being fed by a chalybeate spring Whittaker (1921) suggesting iron rich waters, a potential source being the nearby Palaeocene with iron being leached during redox reactions and then oxidising in the spring. The chalk is entirely overlain by the Palaeocene in this area and it is not known if this spring represents a chalk karst spring or a contact spring developed entirely within the Palaeocene.

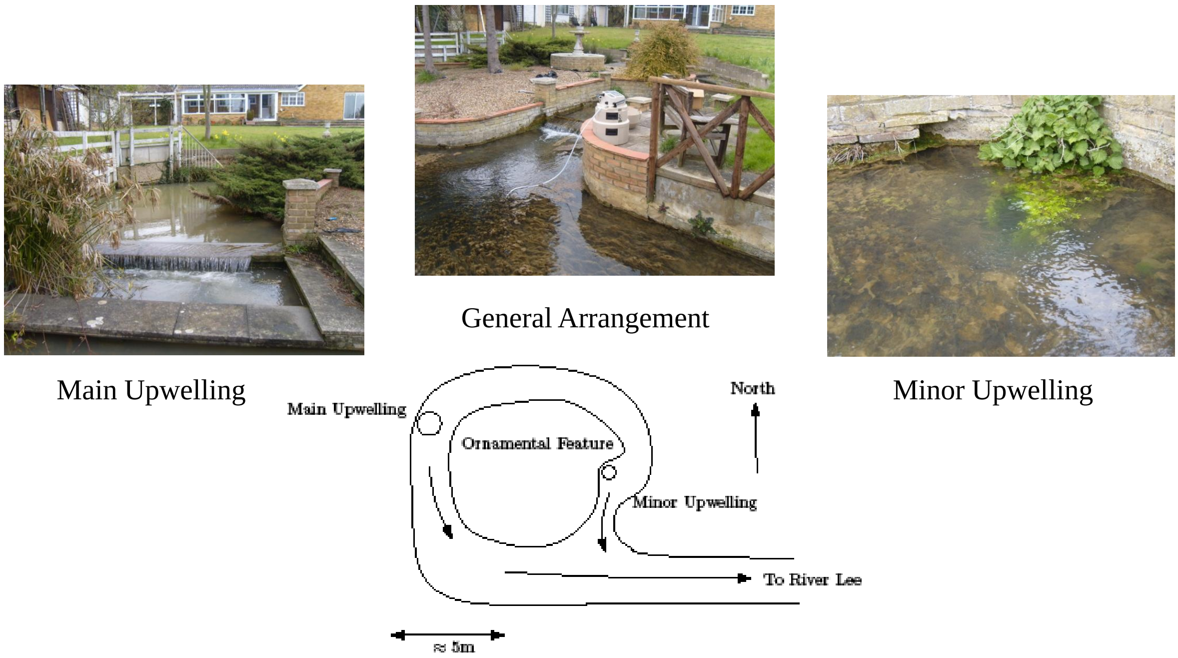


Figure 4.16: General arrangement of the features at Lynchmill Spring

The Lee Valley springs (and those at Woolmer's park) all appear to occur at the edge of the relatively flat flood plain of the River Lee at the base of the eroded Chalk escarpment. This suggests a number of potential hypotheses for their origins (Figure 4.17).

- The springs may originate as gravity driven seeps draining the escarpment slopes; this would explain why they are all located at toe of the slope where water table drops down to meet the level of the River.
- They may represent contact springs on heterogeneities in the chalk which might be acting as aquicludes such as marls or flints that have been exposed by erosion of the River Lee.
- They may occur where conduits and solution enlarged fractures have been exposed by erosion of the River Lee. The description of well defined fissures in the base of the Chadwell Spring depression would lend evidence for this and the differing elevation of springs could be indicative of the dip of the base level of conduit development throughout the aquifer.
- It is possible that one or more of these hypothesis may be acting together

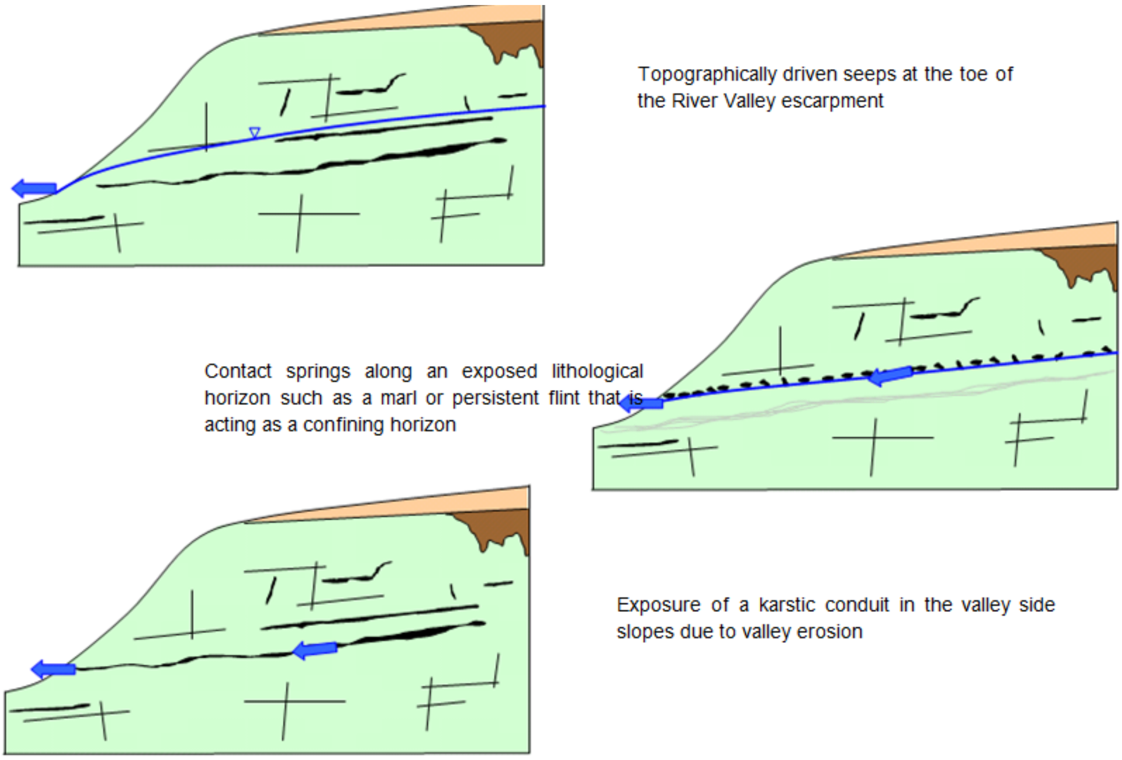


Figure 4.17: Possible origins of the Lee Valley Springs

Table 4.3: Regional Water Chemistry types identified by Hydrotechnica (1988)

Water Type	Key Characteristics	Probable Origin
IA	Calcium Bicarbonate with low K and Mg	Background regional groundwater
		High Calcium, sulphate and nitrate may indicate recent recharge
II	Low Alkalinity, High pH, generally high NO_3, SO_3, Cl and Na	Recent recharge/surface water run off
III	Very low to negligible nitrate	Mature Groundwater from confined aquifer
IV		Polluted Groundwater
V	Intermediate between Type I and II	Mixed Groundwater

4.4 Inference of Karst Development from Groundwater Chemistry

Variations in the natural chemistry of groundwaters can be used to infer a range of information about the processes and transport characteristics in operation since the water chemistry will be diagnostic of the path it takes through the aquifer. A hydrogeochemical survey of the Hertfordshire Chalk aquifer, with particular reference to the Northern New River (NNR) Boreholes operated by Thames Water was undertaken in the mid to late 1980's by Hydrotechnica (1988) and has been supplemented by more recent investigations by (Buckle, 2005). The survey identified 5 distinctive water types present in the aquifer, the characteristics of which are presented in table 4.3.

All the waters within the bromate-affected area are either Type I, Type II or Type V, indicting that confined flow in the chalk does not provide generally provide water to the Northern Lee Valley Wells. (Assem, 2005) determined the ratio of Type IA and Type II water for each of the TWUL wells in the Lee Valley, these data are summarised in Table 4.4.

The wells receiving a high proportion of Type I waters coincide with areas receiving water from the Chalk outcrop and recharge areas, largely thought to be derived from the north and northwest. Type II waters reflect characteristics of the surface waters of the catchment and are typified by the composition of the Mymmshall Brook water but also might be due to influence of the Lee, Colne and Mimram Waters.

The northernmost wells show the most characteristic Type I waters and Broadmeads PWS and Amwell End PWS show distinct water quality with Low sodium, potassium and Chloride and are close to 100% type IA water, that inferred to be from diffuse chalk recharge perhaps from the north and northeast of the River Lea.

Amwell Hill PWS, Amwell Marsh PWS and Rye Common PWS appear to be of similar type but with a higher proportion of Type II water. This has interesting implications for Chadwell spring which has previously considered to be fed mainly from the South west and possibly with a relatively high surface water and karst contribution. It might suggest that whilst the general baseflow to the spring may be derived from the chalk to the north, whilst periodic flow might be fed from the surface water, either of the Lee or from the karstic recharge network of the Mymmshall Brook.

Further south, Hoddesdon PWS, Broxbourne PWS, Middlefield Road PWS and Turnford PWS) are typically $70 - 80\%$ Type IA. Turnford and Broxbourne being of very similar type and possibly influenced by local Type II recharge from Palaeocene deposits (Robinson and Buckle, 2004) but could also suggest a possible component of recharge derived from the Mymmshall Brook catchment.

At Hoddesdon the proportion is close to 60% Type IA, and suggests that a proportion of their water is either derived from relatively close surface sources and run-off such as the Lee Valley and possibly tributaries and Palaeocene run-off or may have a high proportion of rapid recharge from karstic sources.

Essendon PWS also shows very similar concentration to New River Sources comprising dominantly Type IA but also a proportion of Type II (Robinson and Buckle, 2004). The Type II water might either be derived from the Lea or from local Palaeocene surface run-off to the south but could also represent a proportion of Type II waters derived from the Mymmshall Brook catchment, possibly via karstic conduits and mixing with the Type 1A water.

The main uncertainty in considering a karst influence upon water chemistry is that although the surface water component to wells can be inferred and is similar

Table 4.4: Relative proportion and range of Type IA water in abstraction wells in the Lee Valley (Assem, 2005)

	Proportion of Type IA water (%)		
Location	Min	Midpoint	Max
Broadmeads PWS	90	95	100
Amwell End PWS	85	92	100
Amwell Hill PWS	70	75	80
Amwell Marsh PWS	65	75	85
Rye Common PWS	70	80	90
Hoddesdon PWS	55	67	80
Broxbourne PWS	65	72	80
Turnford PWS	65	77	90

to that of the Mymmshall Brook, and other swallow hole drained catchments, the water chemistry is not distinct enough to infer an exact origin. Surface water may enter the ground at a variety of swallow hole locations and may not even be of karstic origin since it could also be derived from more diffuse Palaeocene run-off or percolation.

4.4.1 Other Water Chemical and Biological Indicators

Variations in trace elements and minor constituents such as isotopes can often be of greater use in characterising the origin of waters since their lower concentrations are more affected by smaller variations in aquifer geochemical conditions. The Hydrotechnica (1988) survey did not identify any clear trends in minor element concentrations except that concentrations of Iron, aluminium, colour, turbidity and fluoride appear to be greater in Type II and Type V groundwater consistent with a greater surface water derived component or contamination.

Rainfall events in Hertfordshire and in particular in the vicinity of the Mymmshall Brook catchment have been correlated with an increase in bacterial numbers and deterioration of water quality at wells and springs in the Lee Valley, particularly; Chadwell Spring, Amwell Marsh PWS and Hoddesdon PWS Harold (1937). Rainfall events also lead to increased turbidity at certain locations (Walsh and Ockenden, 1982; Wooldridge, 1920; Kirkaldy, 1950) and occurs at frequently at Essendon PWS where it occasionally causes temporary shutdown of the well but also at Arkley Hole Spring, North Mymms PWS, Rye Common PWS Chadwell Spring and Lynchmill Spring and may be occurring at other springs and wells in the Catchment.

Tritium concentrations presented by Assem (2005) from the Lee Valley abstraction wells are typically $\leq$ 10Bq/l ($\leq$ 85TU) indicate recent recharge. However, it was not possibile to discern any spatial trends on the basis of tritium concentrations.

Table 4.5: Results from the 1927 Tracer injection at Water End (after Harold, 1937)

Observation Point Point	Distance (m)	Observation Time First (hours)	Last	Apparent straight line velocity (m/day)
Chadwell Spring	15,081	69	165	5245
Emma's Well	16,340	76	172	5160
Amwell Hill PWS	16,030	95	172	4049
Amwell Marsh PWS	16,586	95	172	4190
Rye House Spring	16,336	96	192	3821
Lynchmill Spring	15,284	96	192	4083
Hoddesdon PS	15,527	No Detection		-
Colne Valley	Not known	No Detection		-
North Mymms PWS	983	No Detection		-

4.5 Tracer Testing in Hertfordshire

The nature of the Water End and Mymmshall Brook swallow holes appears to have been known at least as far back as 1867 (Harold, 1937) and possibly far earlier. However, prior to the 1920's little was known about the destination of the water entering the swallow holes. Opinion was divided about whether it entered the Lee following dip to the south east, along strike to the northern Lee Valley, or to the Colne catchment in the North and west.

The earliest record of tracer test of the Hertfordshire karst, was undertaken by J.M. Wood sometime prior to 1920 (in Whittaker, 1921). Fluorescein was added to the Mymmshall Brook upstream of Water End swallow at a time of "moderate flow" in the Mymmshall Brook with observations made at springs and wells in the Lea Valley. However no dye was detected; this was interpreted as the dye being transported North East to the Colne. It is not stated if any observations were made in the Colne catchment and consequently this was not confirmed.

A series of tests were undertaken by R.E. Morris and C.H. Fowler in the late 1920's and early 1930's with the primary purpose of investigating possible pollution sources identified in the Northern New River Wells of the Lee Valley and are described by (Lee Conservancy Board, 1935) and (Harold, 1937). These tests have been widely cited as one of the best examples of karst development in the chalk aquifer and are of particular relevance since they cross-cut the bromate-affected area of aquifer.

4.5.1 December 1927 Test

Between 7th December 1927 and 10th December 1927 injections of approximately 454g of Fluorescein dye were added to the Mymmshall Brook twice a day just to the south of the main swallow hole complex at Water End. The total injection mass was approximately 3628g. Observations were made at a number of abstraction sources in the Lee Valley as well as on the Colne. The results of the test are presented in Table 4.5.

Tracer was first detected at Chadwell Spring and observations then occurred in approximately processional sequence downstream along the Lee Valley, except for at Amwell Hill PWS which is located upstream of Emma's well Spring, where detection occurred approximately 20 hours after the spring. A possible explanation for this apparent delay may be such that the spring is fed directly from the Karstic network.

Flow to the pumping stations might also be affected by the prevailing pumping regimes zones of influence of the wells. The degree of interaction with the karstic fracture network might also vary depending upon the prevailing conditions and water table elevations which are unknown. It is possible that the apparent delay might indicate flow arriving via slower flow in non karstic fractures.

Tracer reached the springs further south at Lynchmill and Rye house at approximately the same time, shortly after it was detected at the Amwell Pumping Stations. It is possible that the similarity in arrival time at these springs might suggest a similar transport route despite there being approximately one kilometre separation between the spring discharges.

The last observation times at each location occur between 77 and 96 hours after the first detection. This is approximately the same length of time over which the tracer was injected into the aquifer and suggests that relatively little dispersion occurred.

The shortest duration of positive observation was at the pumping stations at Amwell where tracer appeared after that at nearby Emma's well but the final observation at these locations was similar. It is possible therefore that there was merely a delay in reaching the well but did not reach the wells due to some retardation or dilution effect or perhaps because the wells were not actively pumping at the time. Alternatively, dilution during active abstraction might also have reduced tracer concentrations faster than at the spring.

These data are presentin in Figure 4.18(a). It should be stressed that the connections indicated are purely conceptual as an interpretation aid and do not necessarily represent the geometry of actual karstic conduits or fractures.

4.5.2 February 1928 Test

A second tracer test was conducted in February 1928; however on this occasion the fluorescein tracer was injected into the Welham Green Bourne on the northwest entrance to the Water End swallow hole complex. Flow conditions are described as being similar to the 1927 test with there being no rain for a week prior to the test. The discharge of Chadwell Spring is described as falling (Harold, 1937) probably reflecting the dry antecedent conditions.

The injection pulse was shorter than in 1927, two doses each of approximately 907g of flourescein were added to the stream half an hour apart between 10:30 and 11:00 on February 23rd 1928 for a total injection mass of 1814g. Observations were made at three locations on the Colne (Colney Heath, London Colney and Colney Street) however as with the 1927 test no positive detections were made in the Colne catchment. Observations were also made at North Mymms PWS approximately 1km south of Water End.

The results of the tracer test as reported by Harold (1937) for the 1928 test are vague and occasionally contradictory. Detection at Chadwell Spring and Emma's Well occurred approximately the same time "first thing in the morning" a subjective term. Harold (1937) suggests a transport time to Chadwell Spring and Emma's Well of 70 hours suggesting that detection occurred around 8:30 - 9:00 on the morning of the 26th February, the last observations being at 17:00.

Detection at Amwell Marsh Pumping Station is reported at 06:45 on the 26th of February, giving a transport time of approximately 68 hours. However, the data table in the report (Harold, 1937) suggests a transport time of 80 hours to Amwell Marsh, which if correct would place it's arrival time at around 16:30 - 17:00, a further contradiction considering the last reported observation at Amwell Marsh PWS was at 16:30. There is clearly an error in the report; however since the original information is unavailable, this cannot be easily resolved.

Rye house spring is also given a vague arrival time of "early in the morning" whilst Lynchmill Spring briefly showed dye at around 11:00.

Given the precise nature of the 06:45 arrival time it is considered that this is probably reliable for Amwell Marsh PWS, whilst the travel time of 70 hours is taken as more reliable for Chadwell Spring, Emma's Well and Rye House. Based upon these assumed corrections to the data, the travel times for the 1928 test are presented in Table 4.6

It apparent from this test that tracer arrival times were very similar across the region and it was inferred that the tracer may have travelled in a fan-like fashion along discrete fissures to each location (Harold, 1937; Buckle, 2002). Travel times were comparable with the earliest arrival times in the 1927 test under similar flow conditions, although there appears to be more consistency in travel time. It is possible that the 1928 test may have been differently affected by the pumping regime in operation, the slight difference in injection point (the Welham Green Bourne) rather than the Mymmshall Brook may also have affected the entrance into the karstic network and as a result the determined flow path and rate.

The timing of last observations suggest that the two pulses of tracer passed the detection points for only a very short duration at Lynchmill spring but for up to 10 hours at Amwell Marsh. This difference in timing spread is likely to be due to tracer dispersion. However, in 1927 the frequency of injection pulses at regular (assumed to be 12 hour intervals) probably merged the tracer pulses into a single observation of dye, had they been recorded quantitatively a multi-modal peaked distribution would probably have been observed with each peak dispersed so that the tracer

Table 4.6: Summarised results from the 1928 Tracer Test from the Welham Green Bourne at Water End (after Harold, 1937)

Observation Point Point	Distance (m)	Observation Time First (hours)	Last	Apparent straight line velocity (m/day)
Chadwell Spring	15,081	70	78	5184
Emma's Well	16,340	70	78	5604
Amwell Marsh PWS	16,586	68.25	78	5837
Rye House Spring	16,336	70	Not known	5627
Lynchmill Spring	15,284	72	72	5119
Colne Valley	Not known	No Detection		-
North Mymms PWS	983	No Detection		-

Table 4.7: Summarised results from the 1932 Tracer Test from the Mymmshall Brook

Observation Point Point	Distance (m)	Observation Time First (hours)	Last	Apparent straight line velocity (m/day)
Arkley Hole Spring	8090	60	Not Known	3310
Chadwell Spring	15,081	89	113	4089
Emma's Well	16,340	91	Not Known	4315
Amwell Marsh PWS	16,586	92	Not Known	5837
Rye House Spring	16,336	70	Not known	5627
Lynchmill Spring	15,284	72	72	5119
Hoddesdon PWS	15,527	79	Not Known	4688
Colne Valley	Not known	No Detection	-	-
North Mymms PWS	983	No Detection	-	-

signals overlapped into a constant low level signal with some minor peaks. As for the 1927 test, indicative inferred connections have been plotted in figure 4.18(b)

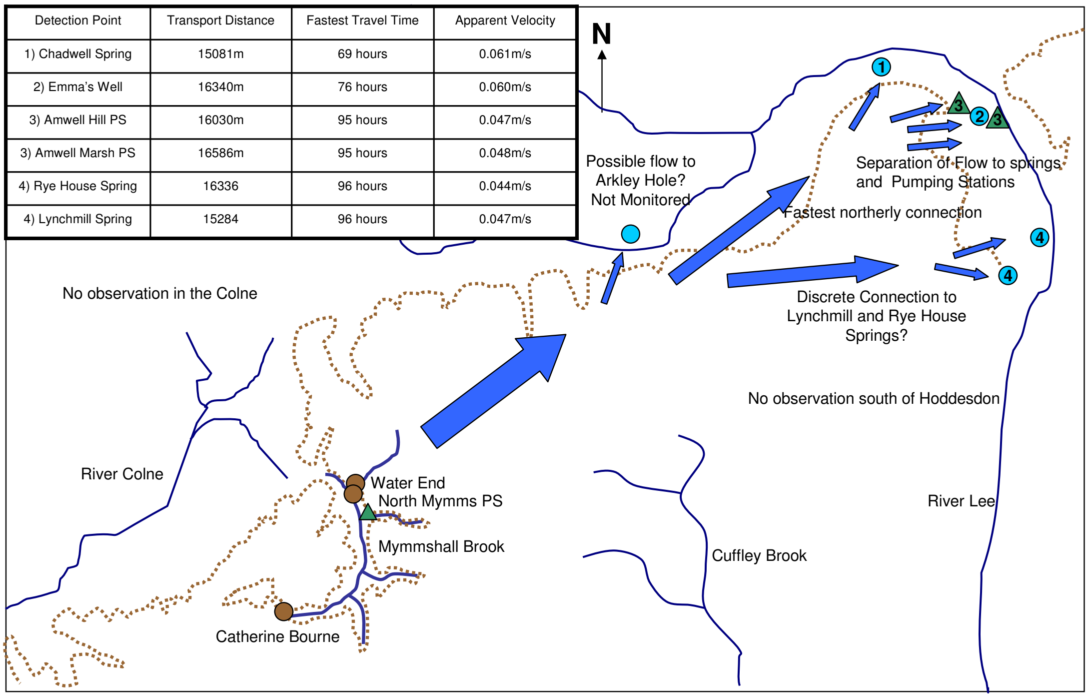
4.5.3 April 1932 Tracer Test

A third tracer test was undertaken in April 1932, flourescein was again introduced into the Mymmshall Brook upstream of the Water End swallow hole complex in a similar fashion to the 1927 test. Approximately 1814g of tracer was injected in four separate doses approximately 15 minutes apart each of 453g of flourescein dissolved in 3.78l (1 gallon) of salt water (Lee Conservancy Board, 1935) the resulting concentration of flourescein in each injection is estimated to be 119.8g/l.

The river flow was estimated to be 0.06m^3/s and was lower than during the 1927 and 1928 tests (Harold, 1937). Assuming even mixing the resulting concentration in the river of the flourescein following each does would have been approximately 7.55g/l. The results of this test are presented in Table 4.7.

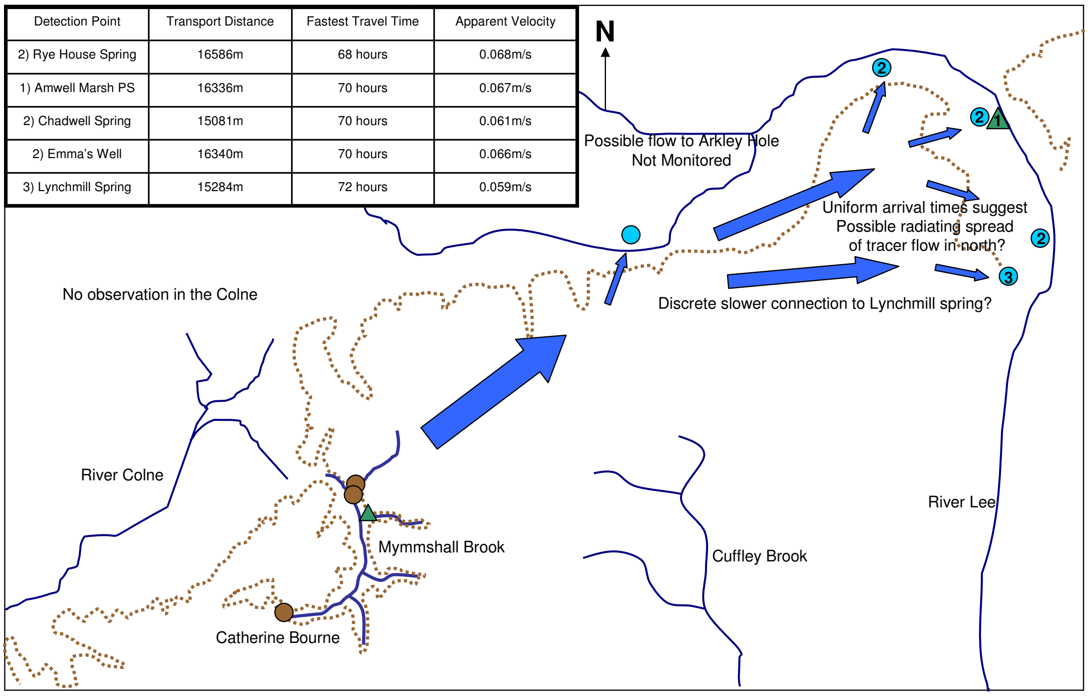
Straight line flow velocities from first arrival times in the 1932 test are slower than in the 1928 test but are generally similar to those recorded in 1927 although are slightly slower for Emma's well and Chadwell Spring.

The earliest detection in 1932 was at Arkley Hole spring, which was not previously monitored for tracer. Arkley hole is approximately half way between Water End and the Northern New River area, it is therefore reasonable to assume that



Detection Point	Transport Distance	Fastest Travel Time	Apparent Velocity
1) Chadwell Spring	15081m	69 hours	0.061m/s
2) Emma's Well	16340m	76 hours	0.060m/s
3) Amwell Hill PS	16030m	95 hours	0.047m/s
3) Amwell Marsh PS	16586m	95 hours	0.048m/s
4) Rye House Spring	16336	96 hours	0.044m/s
4) Lynchmill Spring	15284	96 hours	0.047m/s

(a) December 1927



Detection Point	Transport Distance	Fastest Travel Time	Apparent Velocity
2) Rye House Spring	16586m	68 hours	0.068m/s
1) Amwell Marsh PS	16336m	70 hours	0.067m/s
2) Chadwell Spring	15081m	70 hours	0.061m/s
2) Emma's Well	16340m	70 hours	0.066m/s
3) Lynchmill Spring	15284m	72 hours	0.059m/s

(b) February 1928

Figure 4.18: Summary conceptual network inferred from the December 1927 and January 1928 tracer tests

the detection at Arkley Hole marked the time at which tracer plume might have passed this point. If this is the case it suggests that there could be a variation in flow velocities across the network with slower flows occurring between Water End and Arkley Hole than from the Arkley Hole area to the Northern New River area.

The next arrivals in relatively close sequence were the Lynchmill spring and Hoddesdon PWS, as with the 1927 test this implies a relatively fast connection to the southern part of the Lee Valley.

Tracer was next detected at Chadwell Spring, Emma's Well then shortly after at Amwell Marsh, as with both the 1927 and 1928 tracer test suggesting that flow to this area and these locations probably followed a similar path.

The last detection was at Rye House Spring shortly after that at Emma's Well and Amwell Marsh. In 1927, tracer reached Rye House with a similar travel time to Lynchmill spring inferring a similar flow pathway. In 1928, detection at Rye House occurred earlier than Lynchmill Spring. This variability might suggest that at Rye House and probably at other locations the flow path is sensitive to the prevailing environmental stresses such as recharge, water level and abstractions.

The only record of a last observation was made at Chadwell Spring where flow continued for some 24 hours after first detection, this suggests longer tracer duration than in the 1928 test but possibly similar degree of dispersion to that of 1927. As for the earlier tests, indicative inferred connections have been plotted in Figure 4.19(a)

4.6 January 1935 Tracer Test

A forth tracer test recorded by Harold (1937) was undertaken in January 1935 and examined flow directions from the Catherine Bourne swallow hole. Initially, approximately 680kg of sodium chloride was added to the Catherine Bourne swallow hole in order to determine if there was a detectable trace in the River Colne (at Otterspool) but also in public supply wells at Bushey and Berrygrove to the southwest in the River Ver Catchment. No apparent increase in Chloride was detected at any location except North Mymms PWS, 3km to the northeast of the swallow hole.

In the second part of the test approximately 1814g of Flourescein tracer was added to the Catherine Bourne Swallow hole. Flow conditions were estimated to be around $0.021 m^3/s$ (Lee Conservancy Board, 1935). The results of the test are presented in Table 4.8 and figure 4.19(b).

First detection of tracer was made at the North Mymms Pumping Station 24 hours after injection and this detection reinforces evidence from the Salt tracer that the flow from the Catherine Bourne swallow hole is directed to the northeast. No detection was made at North Mymms PWS in any earlier tracer test indicating that there may not be any southerly component of flow from Water End. North Mymms PWS was not in operation at the time of the 1935 test. It is possible that during

Table 4.8: Summarised results from the 1935 Tracer Test from the Mymmshall brook directly upstream of Water End (after Harold, 1937)

Observation Point Point	Distance (m)	Observation Time (hours) First	Last	Apparent straight line velocity (m/day)
Arkley Hole Spring	11,400	144	Not Known	1914
Chadwell Spring	18,247	163	113	2690
Emma's Well	19,288	No Detection		-
Amwell Marsh PWS	19,490	149	Not Known	3145
Rye House Spring	18,960	144	Not known	3175
Lynchmill Spring	17,731	Not Known	72	3020
Hoddesdon PWS	18,033	142	Not Known	3047
Colne Valley	Not known	No Detection		-
North Mymms PWS	2921	24	Not Known	2983

pumping conditions the path taken by the tracer might vary from that indicated and the whole of a tracer entering the Catherine Bourne swallow hole could be captured by the North Mymms well.

Detection occurred almost simultaneously at Hoddesdon PWS and Lynchmill Spring in the central Lee Valley shortly followed by an arrival at Rye House Spring. The close timing of tracer arrival in this area suggests there could be a discrete more southerly route from the Mymmshall Brook Catchment to the Hoddesdon area that is perhaps intermittently linked to the Rye House Spring but is distinct from that feeding Chadwell Spring.

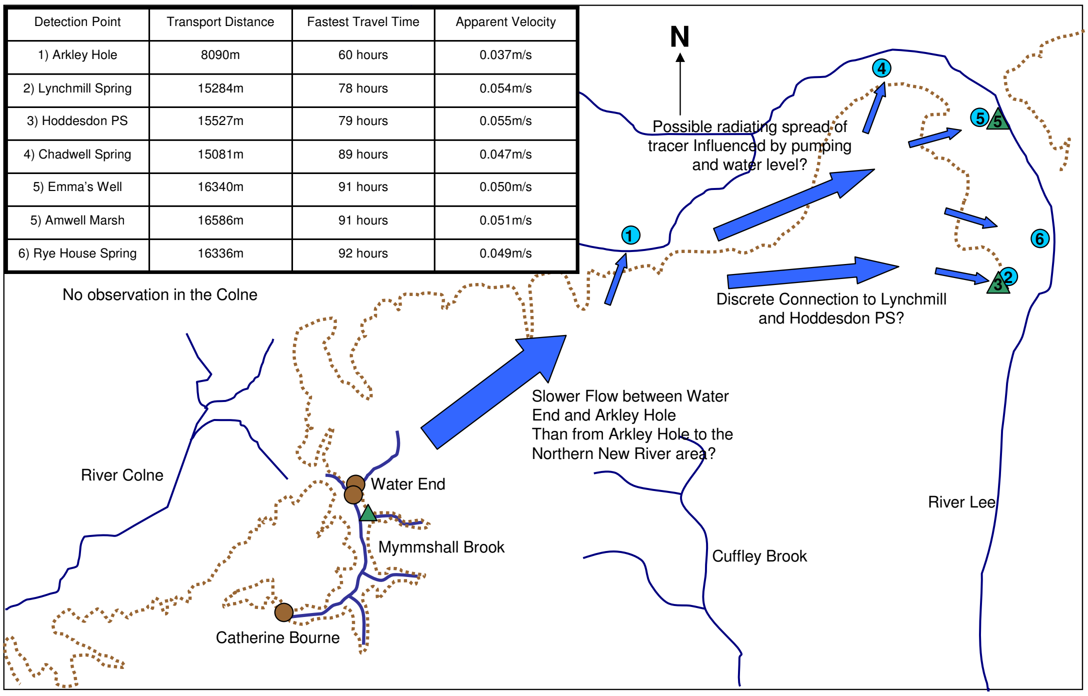
Near simultaneously to the Rye House Spring arrival the first detection was made at Arkley Hole Spring. Transport to Arkley Hole appears considerably slower than in the earlier tests and could suggest that it might not be directly connected to the Catherine Bourne swallow hole or that flow has a more tortuous flow path. Flow to the spring may have been in a less transmissive northerly direction, particularly as it is much closer to the Catherine Bourne than the Lee valley locations where earlier breakthrough occurred. A similar explanation is suggested for the transport to Chadwell spring where only a weak tracer detection was made much later than at any other location.

The test followed a period of two very dry summers and it is inferred that this resulted in more dispersion of the tracer into the non karstic chalk, accounting for slower transport times. It was suggested that the solution-enlarged network may only operate at times of relatively high water level when deeper fractures are surcharged (Harold, 1937).

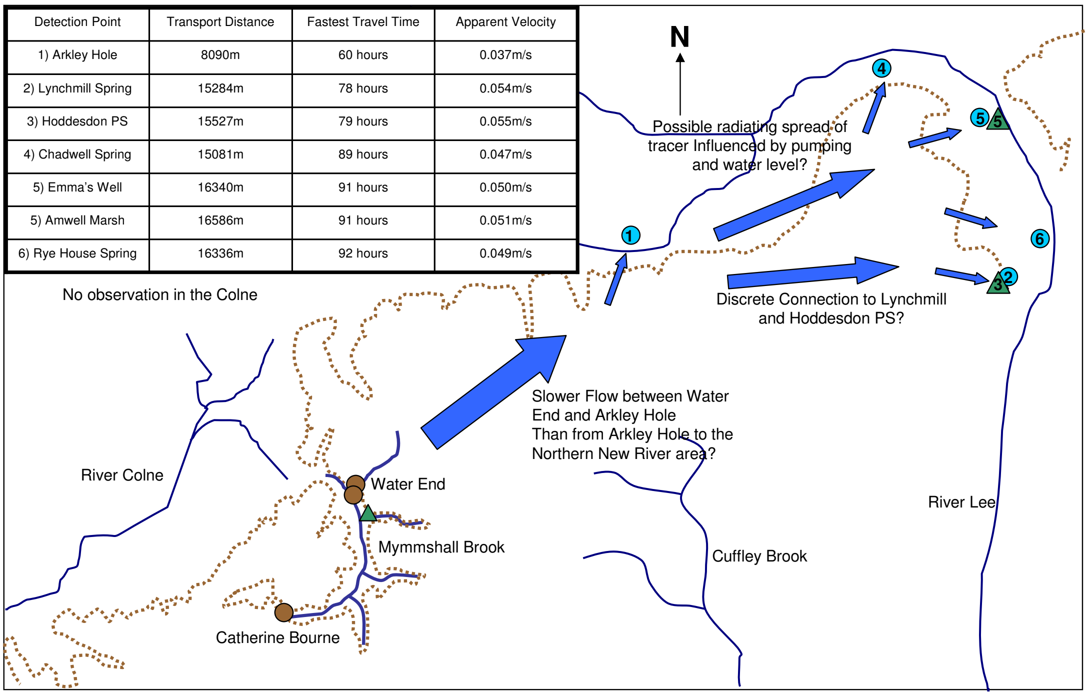
4.6.1 Discussion of Tracer Test Results

A summary plot of first arrival times and last observation times for each of the tracer tests are presented in figure 4.21, all identified connections from tracer tests are illustrated on the network diagram in figure 4.20.

All four tracer tests indicated similar general results; tracer injected into swallow



(a) April 1932



(b) January 1935

Figure 4.19: Summary conceptual network inferred from the April 1932 and January 1935 tracer tests

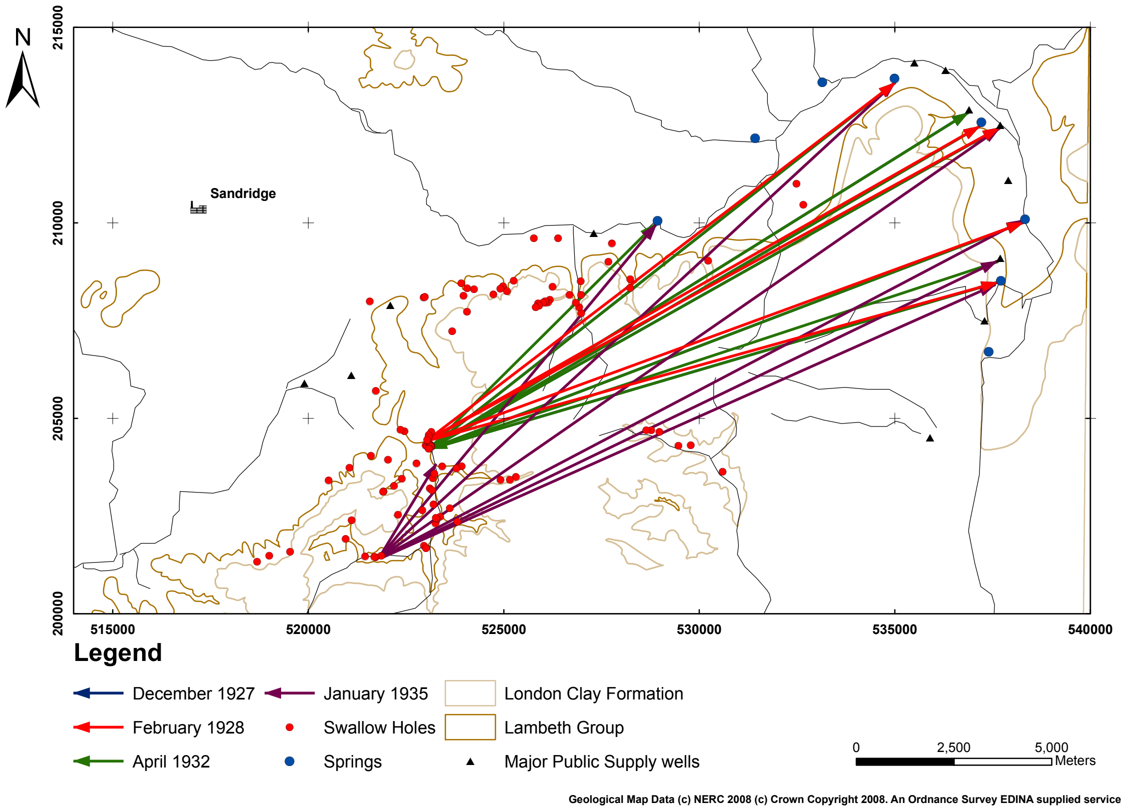
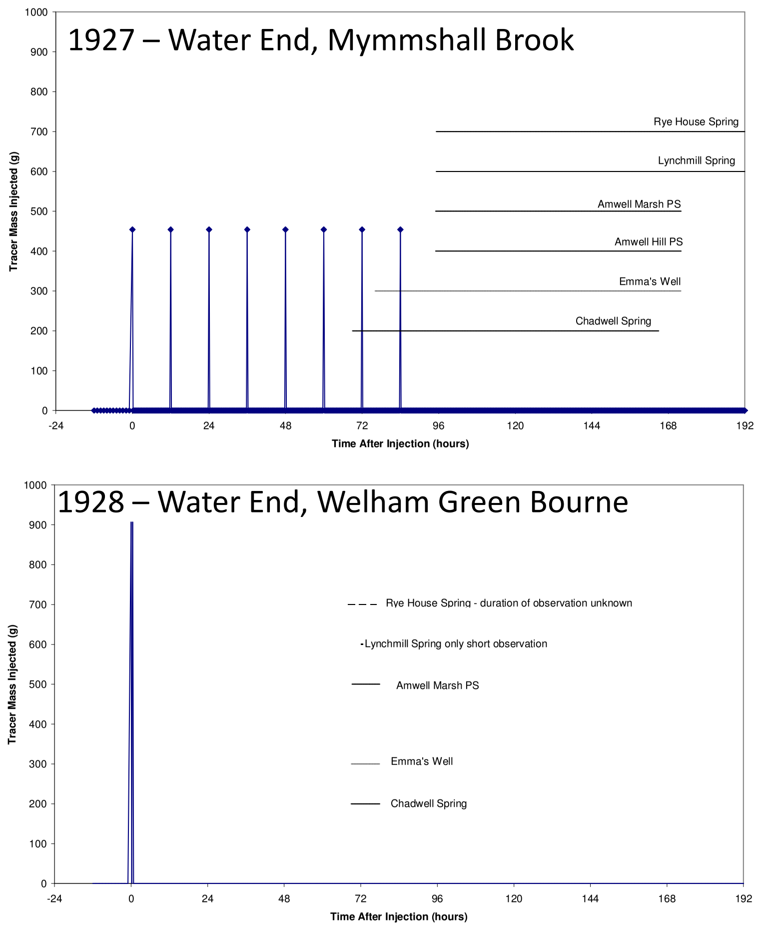
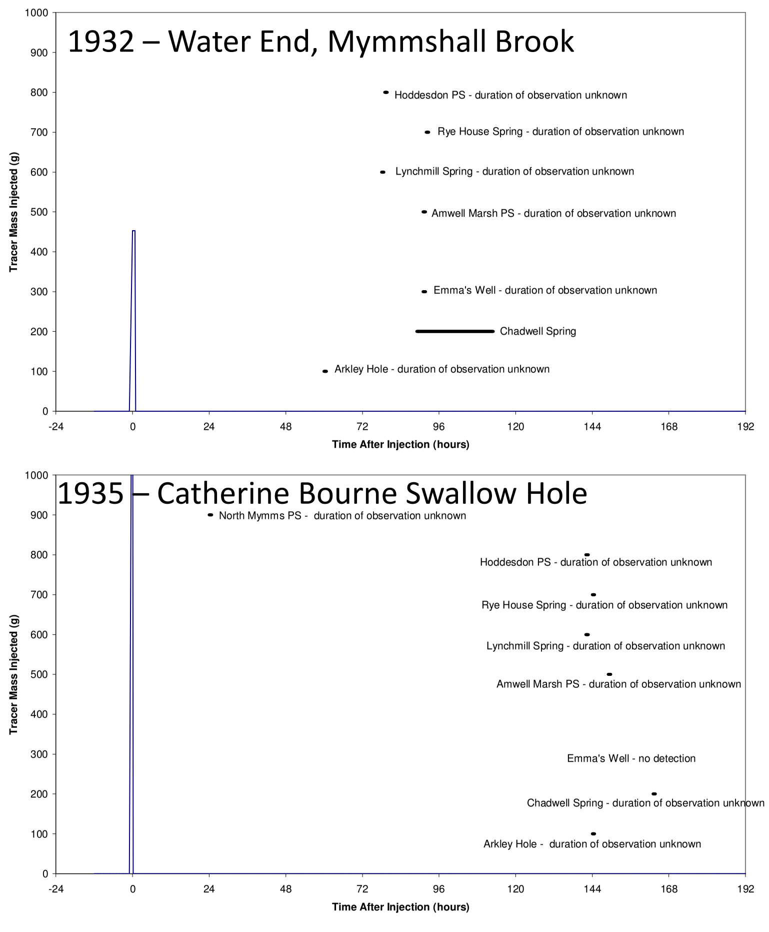


Figure 4.20: Summary of Proven Connections from the 1920's and 1930's tracer tests

holes within the Mymmshall Brook Catchment showed rapid flow connections to springs and wells in the Lee Valley. Tracer was not detected in the catchment of the Colne or the Ver and was only observed at North Mymms PWS when injected into the Catherine Bourne Swallow Hole to the southeast of the well. The implication being that the karstic flow system imparts an apparent anisotropy to flow towards the Lee Valley.



(a) 1927 and 1928 tests



(b) 1932 and 1935 tests

Figure 4.21: Summary plot showing tracer injection pulses duration of observations at monitoring points for the 1920s and 1930s tracer tests from the Mymmshall Brook Catchment.

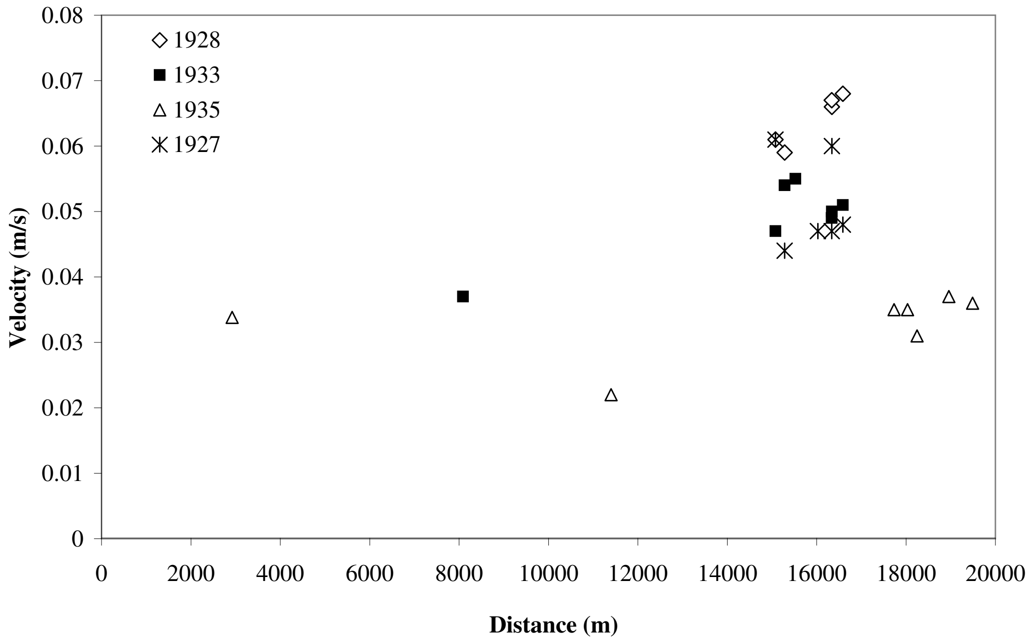


Figure 4.22: straight line tracer velocity with distance for the 1920s and 1930s tracer tests, there appears to a slight increase in apparent straight line travel time with distance

Inferred flow velocities were rapid, typically of the order of 4000 − 5500m/day even for the last observations and are indicative of karstic, and possibly turbulent flow. The apparent duration of observations also suggests dispersion was relatively low, although given the lack of quantitative observation this cannot be confirmed.

A velocity-straight line distance plot suggests that the flows are consistent with that for other karstic carbonate aquifers (Worthington, 1994) who established a mean velocity of 0.022m/s from 2287 tracer tests. The data also indicate that for the Water End injections (1927-1932) there is a slight increase in apparent straight line velocity with distance from injection, although this trend is less apparent for the 1935 test. However, given the uncertainties with timing of arrivals, it is difficult to be certain if this represents a genuine hydraulic effect.

The inferred connections and travel times are not completely consistent between each test and probably reflect sensitivity to environmental stresses which could include but is not restricted to; preceding rainfall, groundwater abstractions, water levels in the aquifer and location of input to the karstic network. Better characterisation is not possible since these data are unavailable for the time of the tracing.

The tracer tests indicate that the karst conduit system extends across the bromate affected catchment, the proportion of flow through the system is non-determined and probably varies depending upon antecedent recharge, groundwater water levels and head gradients. The degree of interaction with the fracture and matrix system is also uncertain.

A major problem with making inferences from these tracer tests are that the observations of tracer appear to have been made by naked eye observation or with

Table 4.9: Estimates of fracture aperture for the 1920s and 1930s tracer tests using the cubic law method. NM=North Mymms PWS, AK=Arkley Hole Spring, CS=Chadwell Spring, AH=Amwell Hill PWS, EW=Emma's Well Spring, RH=Rye House Spring, HD=Hoddesdon PWS, LS=Lynchmill Spring

	Aperture Estimate (mm)								
Year	NM	AK	CS	AH	EW	AM	RH	HD	LS
1927	-	-	7.33	6.45	7.24	6.45	6.49	-	5.80
1928	-	-	7.34	-	7.59	7.68	7.65	-	6.71
1932	-	5.26	6.45	-	6.60	6.65	6.54	6.57	6.43
1935	3.07	3.96	5.04	-	-	5.37	5.42	5.03	4.97

the assistance of Ultra Violet light. A positive result was only achieved when the flourescein was at sufficient concentration to be visible to the following a dilution by the transport processes. It is therefore likely that flourescein might have been present at below visible concentrations both prior to and following the recorded observation times and might even have been present where a positive visual concentration was not made. A further disadvantage is that the observations are qualitative and digital, that is only a positive or negative result was recorded rather than an absolute concentration of dye measured by the intensity of the dye fluorescence.

Although flow velocity and connectivity are the only quantitative data available for these tracer tests, the method of Price (1987) using the cubic law (see section 3.4) allows an estimate of fracture aperture to be obtained using the flow velocities and an estimate of the hydraulic gradient; this has been taken to be the difference in elevation between the input swallow hole and output spring, or where a well is the observation point, the rest water level at the well, and 1.5 times the straight line distance to account of sinuosity of flow path (Field and Nash, 1997). The results are presented in table 4.9.

These estimates of fracture aperture from these data are consistent with that derived for similar swallow hole tracer tests by Atkinson and Ingle Smith (1974) and Banks et al. (1995) and suggest possible evidence that fracture enlargement has occurred. However, the cubic law assumes a single idealised parallel smooth opening, in reality a network of solution enlarged, probably irregular and rough fractures or conduits is probably present. These additional complications in the geometry of fractures means that cubic law estimates do not directly relate to actual field conditions and represent a simplified lumped parameter (Aydin, 2001). Aperture estimates allow determination of the Reynolds number (R_e) which in combination with the relative roughness of the opening determines if flow is laminar or turbulent (De Marsily, 1986). The Reynolds number for flow in a pipe is given by equation 4.8.

$$R_e = \frac{Vd\rho}{\mu} \tag{4.8}$$

Where V is the mean velocity of the fluid, d is the diameter and μ/ρ is the fluid kinematic viscosity. Where flow is within a fracture rather than a pipe like feature

Table 4.10: Estimates of Reynolds Numbers for the 1920s and 1930s tracer tests. NM=North Mymms PWS, AK=Arkley Hole Spring, CS=Chadwell Spring, AH=Amwell Hill PWS, EW=Emma's Well Spring, RH=Rye House Spring, HD=Hoddesdon PWS, LS=Lynchmill Spring

	Reynolds Number								
Year	NM	AK	CS	AH	EW	AM	RH	HD	LS
1927	-	-	685.5	466.7	664.4	473.8	460.6	-	265.94
1928	-	-	685.5	-	766.5	798.8	783.92	-	606.7
1932	-	297.84	463.6	-	505.4	518.9	490.3	552.9	531.2
1935	159.85	133.2	239.1	-	-	295.8	306.6	269.2	265.9

such as a conduit, the pipe diameter d is replaced by a the hydraulic diameter (D_h) of the fracture (equation 4.9) (De Marsily, 1986).

$$D_h = \frac{4S}{p} \tag{4.9}$$

Where S is the cross sectional area of flow through the fracture and p is the outside perimeter of the cross section, which for long fracture traces $Dh = 2a$ where a is the fracture aperture (De Marsily, 1986). Assuming the fracture apertures presented in table 4.9 represent flow in large continuous fractures (for example bedding plane fractures) where $Dh = 2a$, Reynolds numbers for the flows are presented in table 4.10 The kinematic velocity of water, assumed to be at $10°C$ has been taken as $1.307 \times 10^{-6}\mathrm{m}^2/\mathrm{s}$ (The Engineering Toolbox, 2009)

Since all the Reynolds numbers calculated are ≤ 2300 for this idealised case they all fall within the empirically derived range for laminar flow, however if conduit flow is assumed flows are likely to be turbulent.

4.7 Summary Discussion

The presence of the Palaeocene Lambeth group associated with the underlying tectonic structure and geomorphological history has led to conditions highly favourable for the development of chalk dissolution features in Hertfordshire. Most dissolution features occur within 1km of the edge of the Palaeocene outcrop between North Mymms and Hertford, the greatest concentration being associated with valley of the Mymmshall Brook. In this catchment the presence of the Lambeth Group combined with an overall thinning of the formation due to structural controls has interacted with the evolution of surface drainage courses to create conditions highly favourable for the formation of chalk dissolution features. A similar, although less well evolved set of circumstances exist for the higher elevation dissolution features in Gobions Wood and the Cuffley Brook to the East. Whilst known dissolution features in these catchments comprises swallow holes and dolines, in part reflecting an inherent bias in their detection, evidence also suggests the presence of dissolution tubules, solution pipes, sheet pipes and solution enlarged fractures and conduits are present in the subsurface.

In the north east of the region, spring discharges appear to be the dominant form of surface karst, and these contribute flow to the River Lee. The springs are highly variable in character, some showing high sensitivity to pumping whilst others are more persistent. There is also evidence for the development of deep karst in wells in the Lee Valley.

Of particular interest is the close association of the high density of swallow holes within the Mymmshall Brook catchment, the structural high of the Hoddesdon Anticline and the apparent elevated water table which forms the North Mymms recharge mound. It is probable that the high density of swallow holes could be influencing groundwater elevations in this region, perhaps by imparting a high proportion of allogenic recharge into solution enlarged fractures which themselves could be exploiting the structural fabric.

Extensional tension fractures on the hinge of the fold dome may be being exploited by acidic waters to form solution enlarged fractures and dissolution pipes. Discrete swallow holes may direct run-off and recharge rapidly to a depth at which more laterally persistent solution features occur. The small size of the features and discontinuous clay-bounded contact with the surrounding aquifer material may limit the influence of soil moisture deficit to recharge and hence bypass flows and effective rainfall entering such features may be high. The recharge mound morphology might therefore be due to an area of relatively high conductivity resulting from the high concentration of dissolution features - the "honeycombed chalk" of Walsh and Ockenden (1982), surrounded by low conductivity, less dissolution-affected chalk. It is also possible that a low permeability barrier, possibly a fault, is present to the east and south east between the area of the Mymmshall Brook and Cuffley Brook (see section 3.4 and Walsh and Ockenden (1982); Bloomfield et al. (2004)). An alternative possibility is that the recharge mound could be a result of surcharged conduits, when the carrying capacity of the highly transmissive conduits is exceeded the relative head within the conduits forces water into the surrounding aquifer thus causing a localised mounding of water levels (White, 2002).

Additionally, the presence of the Lambeth Group sands and gravels as well as clay-filled dissolution features (such as pipes and chimneys) in the area may hold water in the unsaturated zone and help to maintain saturation in the surrounding chalk (Warren and Mortimore, 2003, e.g.). There may also be a proportion of gravity driven flow along bedding fractures parallel to dip of the dome that may help sustain flow to the rest of the aquifer even in the absence of recharge.

Deeper chalk dissolution features recorded in outcrop at Castle Lime Works Quarry and to a more limited extent at Water End do give some indication of the hydrodynamic characteristics of the features. Of particular interest are the sand filled sheet pipes and associated dissolution tubules seen at Castle Lime Works and the solution enlarged fractures and "caves" and enlarged fractures present at Water

End. These features are more laterally persistent than discrete solution pipes in the upper surface of the chalk at least extending for 10's of metres and are likely to be of greater significance for the properties of the aquifer on a regional scale.

Two types of water have been identified by major ion chemistry, Type IA reflecting background groundwater and Type II reflecting recent recharge and surface waters and in particular sinking streams. A mixture of the Type IA and Type II waters is discharged from springs and wells in the Lee Valley suggesting a blending of more diffuse recharge with the allogenic input of the karst. Surface water is more concentrated in the southern most wells such as Hoddesdon PWS, Broxbourne PWS and Turnford PWS implying a greater karst contribution. Mixing of the two water types could also potentially enhance the development of solution within the aquifer.

Tracer testing from the Mymmshall Brook catchment indicated rapid flow velocities and connections over large distances consistent with flow in discrete solution enhanced fractures or karst conduits. The difference in timing of tracer arrival at springs suggested by the tracing suggests there could be at least two distinct, and possibly more, main flow routes:

- a northern component feeding Arkley Hole and the Northern New River trending from Water End towards Chadwell spring sub-parallel to and close to the Palaeocene feather edge
- a more southerly component towards Hoddesdon and the Lynchmill spring, possibly with a more direct connection to the Catherine Bourne Swallow Hole.
- The may also be slower transfer of water between the two main flow components.

Tracer testing indicates an apparent anisotropy in the destination of groundwater flows from within the Mymmshall Brook catchment to the northeast, despite the steepest hydraulic gradient away from the North Mymms recharge mound occurring sub-parallel to bedding toward the southeast, this is discordant with the regional flow directions (see section 3.6) which is generally sub-parallel to bedding. If solution enhanced fractures and conduits are laterally persistent in the subsurface beyond the Mymmshall Brook catchment the high transmissivity of such features would tend to dominate the flow regime and lead to a flattening of the head gradient, which is consistent with that seen east of Essendon.

The generally accepted conceptual understanding of the function of the Mymmshall Brook - Lee Valley karst system based on the tracer tests (e.g. Walsh and Ockenden, 1982; Buckle, 2003, and others) is that a network of solution enhanced fractures and or conduits extends in a north easterly direction from the Mymmshall Brook catchment and distributes flow to wells and springs in the Lee Valley. Variation in the timing of tracer arrivals and apparent flow paths is attributed to varying water level conditions within the karstic system which cause different tortuous flow paths to operate. Whilst such a model could explain the observations it also raises several questions, particularly relating to how such a system could evolve:

- Regional flow directions, as inferred from groundwater contours and the general distribution of bromate contamination suggest a close association with both bedding and structure, flow paths from the tracer testing developed in a north easterly direction approximately aligned sub-parallel to the Hoddesdon syncline and are consistent with regional fracture fabrics. Synclines also tend to focus groundwater flow along their axis rather than cross cut it and therefore it is uncertain how a connection could have developed to the springs at Arkley Hole, Chadwell Spring and Emma's well to the north of the syncline axis. One possibility is the inferred presence of N-S faults associated with valleys and swallow hole clusters on the Paleocene-Chalk boundary.

- A major uncertainty is how solution enlargement of these fractures occurred over such a large distance ($10km$) below a relatively impermeable cover of London Clay with only limited allogenic recharge from swallow holes of the Cuffley Brook, south of the apparent straight line between the Mymmshall Brook and the northern Lee Valley. Younger (1989); Lloyd and Hiscock (1990); MacDonald et al. (1998) all suggest that solution enhancement would be restricted below thick cover deposits, and would tend to be restricted to outlet points.

- This conceptual model does not consider swallow holes and dolines developed along the Palaeocene feather edge and how flow into these features relates to the general distribution of karstic flows.

The regional fracture sets are oriented sub-horizontally along bedding with a dip to the south east and a dominant sub-vertical NW-SE aligned set and a subordinate NE-SW aligned set. The apparent anisotropy is consistent with preferential enlargement of the NE-SW aligned set below and adjacent to the Palaeocene outcrop to which it is sub-parallel. This alignment is possibly a result of past fluvial and glacial hydrology preferentially exploiting pre-existing fractures and could be linked to the course of the "Proto-Thames" which flowed through the Vale of St Albans sub-parallel to this orientation. The Thames and the Anglian Glaciation are likely to have been associated with a large amount of groundwater flow and would have acted to control flow directions in an approximately concordant fashion. This may have led to exploitation of the NE-SW fractures and groundwater movement along strike intersections with bedding rather than down-dip in a NE-SW orientation in the area adjacent to the Vale of St Albans.

A preliminary conceptual understanding of the function of the Hertfordshire karst based upon this review is presented in figure 4.23.

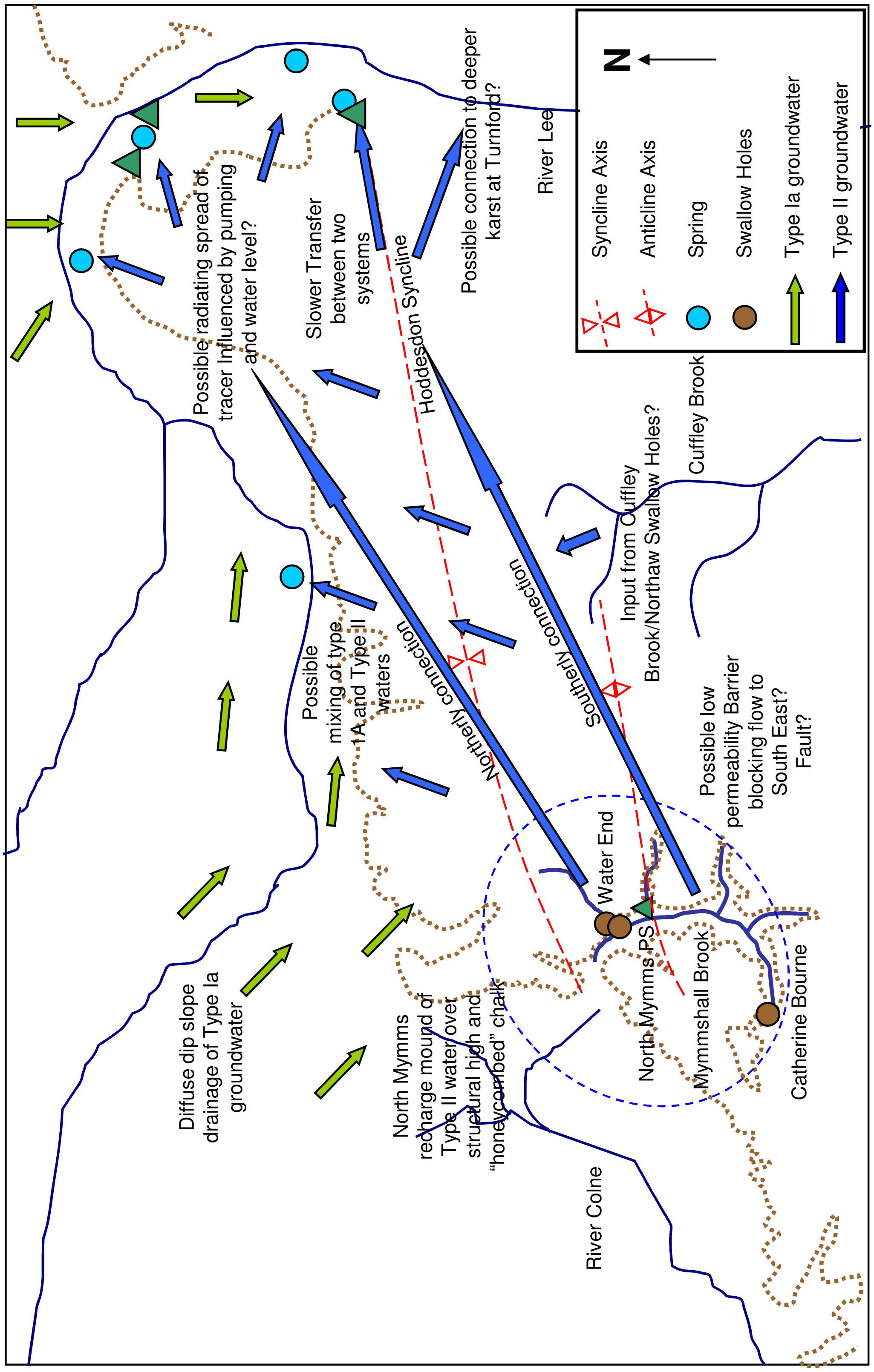


Figure 4.23: Initial conceptual understanding of the Hertfordshire Karst Flow system

4.7.1 Implications for Transport of Bromate

The principal aim for carrying out this review of the karstic hydrogeology of the Hertfordshire chalk is to establish the potential influence the karstic system may have on the transport of Bromate from the Sandridge area towards public supply wells in the Lea Valley.

The existence of the North Mymms Recharge Mound appears to be important in controlling groundwater flow directions in the Hatfield area and also acts as a catchment boundary forcing the regional flow further north and eastward along the course of the River Lea rather than southeast into the London Basin as might be expected from the regional dip. The existence of this mound and its seasonal variation might therefore have influenced the evolution of the bromate plume and in particular might be a factor contributing to the observed plume dog-leg east of Hatfield.

If a NE-SW aligned solution enlarged fracture system has developed due to the influence of the karstic system it might reasonably be expected to have some influence on the transport of bromate within the area that such anisotropy exists. As a straightforward observation based upon what is known from the tracer tests it might be expected that bromate laden groundwater entering a karstic fissure in the area east of Hatfield is directed northeast towards the area of Chadwell Spring and Emma's Well. However, observed concentrations of Bromate in this area are generally lower than occur further south in the Lee Valley.

It is possible that the lower concentrations might reflect dilution by unpolluted groundwater derived from further north, however there are a number of other indications that the southern Lee Valley wells (Rye Common, Hoddesdon, Middlefield Road, Turnford and Broxbourne) have a karst component:

- Trend analysis suggests that Essendon PWS, Hoddesdon PWS, Broxbourne PWS and Turnford PWS show similar trends in bromate concentration with time and as a response to recharge (Robinson and Buckle, 2004).
- Deep Karst (140mbgl) has been identified at Turnford
- Assem (2005) inferred a higher proportion of Type II water at Hoddesdon
- Tracer Tests indicated a possible distinct connection to The Lynchmill Spring, Hoddesdon and Rye House Springs compared to that at Chadwell Spring and Emma's Well

East of the Essendon area the observed occurrence of bromate in groundwater sources is sporadic and inconsistent and as a result it is difficult to define a dispersed contaminant "plume". It is possible that this reflects bromate movement along discrete fractures or fracture networks, that may not necessarily be intersected by abstractions or observation boreholes. It has already been shown (see section 2.1) that Essendon PWS and Arkley Hole spring show similar magnitude and variation of bromate concentrations and suggests that both locations may intersect a similar flow pathway.

Of the abstraction locations (both public and private) monitored in the Lee Valley only the public water supply locations, that is those with adits and/or a high transmissivity and discharge show concentrations of bromate at detectable limits. Could this imply that the wells and or adits intersect highly transmissive solution enhanced fractures and/or conduits bearing bromate laden water? It is possible that the adits were constructed intentionally to intersect such features, long term abstraction and localised aquifer enhancement within the vicinity of the wells might have further enhanced connection to the karst flow network.

If rapid transport occurs within discrete conduits between Hatfield and the Lee Valley approximately sub-parallel to the feather edge of the Palaeocene, rapid changes in the fracture concentrations might occur, especially following recharge events. The rapid connectivity of the swallow holes to the water table is likely to imparts a rapid response following rainfall to areas of the catchment that receive a karstic contribution. This might have an effect on observed concentrations in supply boreholes that are known to have a karstic contribution such as Hoddesdon and Turnford. Fitzpatrick (2007) attempted to identify a statistical correlation of estimated stream input to the Water End swallow holes, based upon the stream discharge of Atkins (2006), and bromate concentrations at public water supply sources. A statistically significant correlation could not be identified however it was recognised that the availability of stream discharge data are limited and may have impacted the analysis.

Typical diffusion times in chalk (Barker, 1993) suggest that for the advection times inferred from the tracer tests of between 3 and 8 days the maximum penetration of any solute into matrix blocks from the fractures is likely to be of the order of only a few cm. In large aperture fractures or conduits this might not even be long enough to allow full diffusion across a fracture aperture. If bromate is being transported in the karst system, it is unlikely that a high degree of dual porosity transfer to the matrix will be occurring, as a result concentrations may be less diluted and dispersed during times of low recharge when these conduits are not being flushed with water from the Mymmshall Brook area. Such a mechanism could explain why concentrations observed at some Lee Valley wells (for example Hoddesdon PWS, Turnford PWS) are of similar magnitude to that at Essendon PWS and greater than would be expected if classical mechanical dispersion (which has been empirically linked to transport distance and flow velocity) is applied.

As an example, an analytical solution to the two dimensional advection dispersion equation for a constant source injection (Bear, 1972) has been used to estimate the likely concentration at Hoddesdon based upon the mean concentration at Es-

Table 4.11: Calculation of theoretical concentration at Hoddesdon PWS (C_{HOD}) assuming a direct flow path from Essendon PWS using an analytical solution to the Advection Dispersion Equation (Bear, 1972). Q/b has assumed to be unity to allow a uniform concentration of 27 $\mu g/l$ throughout the aquifer section. $^{*}D_L$ has been calculated using the relationship derived by Xu and Eckstein (1995) - $\alpha_L = 0.83((\log(x)))^{2.414}$, where α_L is the longitudinal dispersivity, and $D_L = \alpha_L \times v_x$. D_T has been taken as 10% of D_T.

x (m)	y (m)	C_0 ($\mu g/l$)	v_x m/day	D_L^* (m^2/day)	D_T (m^2/day)	K_0	C_{HOD} ($\mu g/l$)
10647	0	27	1700	40732	4073	3.13×10^{-98}	2.8×10^{-5}

sendon assuming two dimensional dispersion and is shown in equation 4.10.

$$C_{(x,y)} = \frac{C_0(Q/b)}{2\pi(D_L D_T)^{1/2}} \exp\left(\frac{v_x x}{2D_L}\right) K_0 \left[\left(\frac{v_x^2}{4D_L}\left(\frac{x^2}{D_L} + \frac{y^2}{D_T}\right)\right)^{1/2}\right] \tag{4.10}$$

Where $C_{(x,y)}$ is the concentration at a distance x and offset y from a flow path, C_0 is the source concentration, Q is the injection rate, b is the vertical thickness of aquifer, D_L and D_T are the longitudinal and transverse dispersion coefficients, v_x is flow velocity in the x direction and K_0 is the modified Bessell function of the second kind and zero order.

It is apparent that observed concentrations at locations in the Lee Valley are higher than would be expected assuming a classical advection and dispersion type transport mechanism alone and suggestive of a rapid transport pathway of limited attenuation existing between at least the Essendon area and potentially further west.

4.7.2 Requirement for a New Investigation

Evidence from a variety of sources indicates that there is karst enhancement of groundwater flow in Hertfordshire and that flow within the system is influencing the transport of bromate over a scale of at least several kilometres. This review raises several questions for future consideration with respect to considering the degree to which bromate-laden groundwater interacts with the karstic system during transport towards the Lea Valley, specifically:

- To what degree does dilution and dispersion occur during transport in the karstic system, can quantitative aquifer parameters be obtained for use in transport models and predictions?

- To what extent does recharge from the karstic system act as a dilution for bromate concentrations in the aquifer?

- How do seasonal variations in recharge and abstraction influence the behaviour of the karstic system and do different routes become active under different hydrological conditions?

- To what depth does the karstic groundwater transport network extend?

- How far northwest does the karst system and the North Mymms Recharge Mound have influence (e.g. at Hatfield)?
- How do spring hydrographs in the Lee Valley correspond to abstraction rates and recharge events in the Mymmshall Brook and does bromate respond in a similar manner?
- Has the mixing of Type 1A and Type II groundwater resulted in mixing corrosion and preferentially aligned solution enlargement of the fracture system?

To begin to address these uncertainties, a new suite of tracer tests was proposed and are described in Chapter 5.

Chapter 5

Catchment Scale Tracer Testing

5.1 Strategy and Objectives

Migration within a karst network is a key mechanism of contaminant transport between Hatfield and the Lee Valley. In order to be able to incorporate this system appropriately in predictive models the hydrodynamic behaviour of the system needs to be evaluated in a more detailed way than historical tracer test data (i.e. Harold, 1937) allow. To further investigate this system, a new suite of catchment scale tracer investigations were conducted.

Developing the tracer test strategy was an iterative process developed in consultation with the Environment Agency, Veolia Water Three Valleys and Thames Water. A number of modifications, particularly with respect to the tracer injection locations were made between the first submitted proposal in July 2007 and the final accepted proposal in November 2007. Many changes were driven by operational constraints of the Water Utilities (e.g. not being able to suspend scavenge pumping at Hatfield PWS) and/or practicalities of the sampling regime. The tracer test described in this chapter reflects the final design of the test, a summary of the preceding proposals from which this test was developed is presented in Appendix B. The overarching objectives of the tracer investigation were as follows:

- Define travel time and connectivity within, and adjacent to the Vale of St Albans. Tracing will test for the possibility of karstic or semi karstic routes developed along the former Proto-Thames corridor beneath the Vale of St Albans.

- Establish the movement of groundwater tracer under the influence of pumping at Hatfield PWS so that mechanisms and hydrodynamic behaviour associated with such "scavenge" pumping can be better understood.

- Establish hydrodynamic parameters associated with connections such as dispersivity and hydraulic conductivity from tracer breakthrough curves.

- Quantitatively repeat historic tracer tests (Harold, 1937) under modern aquifer and groundwater conditions.

The data obtained can be used to improve, calibrate and validate existing and future groundwater flow and transport models of the affected region of aquifer as wells as delineate the spatial extent of karstic flow mechanisms. A formal proposal, developed in accordance with the recommendations of Ward et al. (1998), outlining the objectives and proposed methods and including a groundwater risk assessment was submitted for Environment Agency, Thames Water and Veolia Water Three Valleys approval in November 2007. Following acceptance of the risk assessment, approval for injecting the tracer into the groundwater was granted from Three Valleys Water on 05/12/07, from Thames Water on 20/12/07 and the Environment Agency on 17/12/07.

5.2 Selection of Tracer and Injection Locations

Tracer investigations of karst systems usually inject tracer directly into swallow holes or other surface karst to establish connectivity and parameters of the conduit system. The initial proposals favoured a location positioned between Hatfield PWS and Essendon PWS (for example into one of the Hatfield Park swallow holes) which appeared to overlie the approximate centerline of the bromate “plume” east of Hatfield. It might also have revealed if Essendon PWS received flow from these swallow holes and informed knowledge of the downgradient influence of scavenge pumping at Hatfield PWS. However, there were concerns about how active the swallow holes were given the relatively small catchment sizes and that tracer might be lost or sorbed in the unsaturated zone and the injection location was moved to the Water End swallow hole complex. A connection between Water End and bromate contaminated locations in the Lee Valley has already been established (i.e. Harold, 1937) and flow into Water End has been speculated to influence the seasonal dilution of bromate concentrations as seen at Essendon, Arkley Hole Spring and the Lee Valley (Buckle, 2002). The quantitative tracing, particularly its westward extent, and would also allow a near direct, but more quantitative duplication, of the previous suite of tests.

The bromate itself acts as a tracer delineating the extent of flow paths from Sandridge to the Lee Valley. Unfortunately the history of contaminant release is poorly characterised and there is insufficient data that can be used to infer quantitative aquifer parameters beyond a connection to the Sandridge area. A second injection location was therefore desired at or close to the bromate source where a known mass of tracer could be injected at a known time to act as a proxy for the transport of bromate. Since there is no apparent or known surface karst development in the vicinity of Sandridge injection would be undertaken using a borehole, this in turn introduced further constraints on identification of a suitable location:

- It should contain relatively high concentrations of bromate consistent with being positioned on a downgradient flow path from Sandridge.
- The borehole would have to not be actively pumped or in use as a regular sampling or observation borehole for bromate since this could introduce the risk of tracer removal and/or cross contamination, particularly in the period immediately following tracer injection.
- Many of the boreholes in the area are relatively shallow (typically with depths $\leq 20mbgl$) and with only limited penetration into the chalk aquifer.
- Allow safe and easy access for injection with associated injection and/or sampling equipment.

The borehole selected was the Harefield House observation borehole (NGR TL177100), positioned approximately $750m$ east-south-east of St Leonard's Court, Sandridge and close to the apparent centre line of the bromate "plume" in this area. It has a mean bromate concentration of 2110μg/l. The borehole is constructed entirely within the Chalk to $\approx$ 25mbgl and is located on the side slopes of the Sandridge dry Valley. The average water level is approximately 15mbgl.

It was also of interest to attempt to delineate both the westward extent of karstic flows from the Palaeocene feather edge and also if possible the capture zone of scavenge pumping at Hatfield PWS. To this end, a third injection location was required within the vicinity of Hatfield and upgradient of Hatfield PWS. Available boreholes with a deep penetration into the aquifer were limited, the selected borehole was located at Comet Way, Observation borehole 5. The borehole is constructed in the fluvio-glacial deposits of the Vale of St Albans and extends approximately $5m$ into the Chalk to $\approx$ 19.6mbgl. It is positioned on the eastern side of Hatfield and is approximately in the centre of the apparent bromate "plume" with a mean bromate concentration of 963μg/l. The rest water level is approximately 15mbgl.

Both the Harefield House OBH and the Comet Way OBH are routinely monitored by the Environment Agency on an approximately quarterly frequency as part of their ongoing bromate monitoring programme. However since both were sampled in early February 20008, approximately one month prior to the injection it was hoped that sufficient migration would occur before they would be re-sampled by the agency in the subsequent monitoring round.

To test the suitability of the selected locations, single borehole dilution tracer tests (SBDTT) (Fitzpatrick, 2008) were conducted in each during January and February 2008 prior to injection. This was to ensure that active flow occurred within both boreholes and establish groundwater velocities. The SBDTT was also

Table 5.1: Summary of tracer injection locations

Location	Easting	Northing	Type (m)	Depth (m)	Diameter	Notes
Harefield House	517748	210035	OBH	25.48	0.05	Slotted PVC casing from 14.65 to 25.48mbgl
Comet Way	521760	208911	OBH	19.6	0.2	Plain Steel Casing to 16.9mbd, slotted steel casing from 16.9 - 19.6mbgl
Water End	522934	204632	Swallow Holes	n/a	n/a	-

used to guide the depth at which tracer was to be injected (see Section 5.6). Summary details of the injection locations are summarised in table 5.1 and their position with respect to the area of bromate affected aquifer is illustrated on on Figure 5.1.

5.2.1 Tracer Selection

The primary constraint in selection of an appropriate tracer for these investigations was the risk of tracer entering public water supply wells leading to a reduction in water quality. To mitigate this risk, three species of bacteriophage (phage) were adopted as tracers. Bacteriophage are a type of virus which can only infect specific bacterial host species are unable to replicate outside of their host bacteria. Phage are invisible to the naked eye and due to their specific nature, they pose no risk to humans or animals.

Phage have been shown to be highly sensitive groundwater tracers since they can be injected at high concentrations (typically $\geq 10^{13}$pfu/ml) and the detection limits for phage are highly sensitive ($<$ 1pfu/ml) (Wimpenny et al., 1972; Keswick et al., 1982; Ward et al., 1998). Phage are non-pathogenic,easily and cheaply detectable with reasonable survivability in groundwater environments and so possess many characteristics of an ideal tracer. However, their use as tracers can be limited by inactivation and under certain conditions the presence of natural background. Bacteriophage have previously been used in a number of groundwater tracer studies in the Chalk aquifer, including tracing to public water supply boreholes (e.g. Skilton and Wheeler, 1989; Price et al., 1992; Maurice et al., 2006).

5.2.1.1 Tracer Characteristics

Processes controlling virus transport, sorption and in-activation in groundwater and the subsurface are relatively poorly understood although a number of studies have investigated various aspects of virus sorption and in-activation in relation to developing suitable viral tracers as surrogates for human pathogens (e.g. Yates et al., 1985; Taylor et al., 2004; Collins et al., 2006). Limited data are available for viral transport and survival in the Chalk aquifer.

Although transport and inactivation rates appear to vary by phage type, higher temperature (Yates et al., 1985) and greater exposure to UV light are considered to be the most important factors in controlling bacteriophage inactivation (Jin et al., 2000). Inactivation and sorption is also influenced by a less degree by other factors such as the presence of groundwater micro-organisms (Gordon and Toze, 2003), soil type (e.g. Funderberg et al., 1981), dissolved O2 unsaturated conditions as well as characteristics of the water chemistry such as pH, electrical conductivity and organic carbon content.

Soils with at least $0.5 - 1\%$ organic matter and at least $1 - 2\%$ clay or silt are most effective at removing viruses from water due to sorption, although the depth or relatively surface area of the soil is also important (Funderberg et al., 1981). The Chalk is relatively free of organic matter being mostly pure calcium carbonate with some clay minerals and thus sorption is most likely to occur in the capping soils, which are dominantly thin, and clay and silt rich, in part being derived from insoluble residue of the Chalk. Sorption might also occur to organic material such as bacterial films on fracture surfaces, and might be more prevalent in surface waters where sorption could occur to plant and other organic matter and might also occur in spring discharge pools. Table 5.2 indicates a summary of the tracer characteristics for the three phage species used in this study.

Sorption of phage is related to their iso-electric point which controls their charge relative to the pH of the medium in which they are immersed, both $MS2$ and $\Phi X174$ are likely to be negatively charged in the pH range typical of Chalk groundwater (≈ 8), and thus will be less strongly sorbed than at lower pH. $MS2$ with a lower iso-electric point will be more strongly repelled by negatively charged aquifer particles such as clay minerals on fracture surfaces compared with $\Phi X174$ and hence is less likely to be sorbed. Flow conditions might also be important in influencing survival of $MS2$ phage (McKay et al., 2002) and Ward et al. (1998) suggest that turbulent flow, as might occur in abstraction well pumps or within karst conduits, could also influence phage survival.

$MS2$ Coliphage is considered to be a relatively conservative phage tracer since it has low absorption to aquifer materials (Collins et al., 2006), although it does show retardation in transport studies in sand columns (Jin et al., 2000) and inactivation at the air-water interface under unsaturated conditions (Thompson et al., 1998). Many studies have investigated the in-activation rate of MS2 Coliphage in groundwater

Table 5.2: Characteristics of the bacteriophage used in this study

Phage	Host	Size (nm)	Inactivation Rate Log_{10}/day
$MS2$	E-Coli, Salmonella	25	0.01-0.068
$\Phi X174$	E. coli. and other Enterobacteriacea	23	unknown
Serratia Marcescens	*Serratia Marcescens* other Enterobacteriacea	50	0.07-0.16

although due to variability in the experimental conditions a wide range of values are reported. Temperature dependent studies by Yates et al. (1985) suggest a value of $0.04 - 0.162\log_{10}$ per day in groundwater at 12^oC. Geo-statistical studies of MS2 phage waste water effluent suggest an in-activation rate of 0.068 to $0.71\log_{10}$ per day (Yates et al., 1986), Laboratory experiments in groundwater by Collins et al. (2006) suggest an inactivation rate of $0.011-0.013\log_{10}$per day whilst a temperature dependent formula provided by (Gerba et al., 1991) suggests an inactivation rate of $0.033\log_{10}$ per day in groundwater based a temperate of 10^oC, typical of that for Chalk groundwater.

$\Phi X174$ phage is the least hydrophobic of all phage (Collins et al., 2006) and is likely to be less strongly sorbed, especially to organic matter. Investigations into sorption of $\Phi X174$ phage indicate little retardation in sand columns (Jin et al., 2000) and that in a range of soil types residence time is a key factor in the sorption of this phage rather than specific properties of the aquifer material (Funderberg et al., 1981). Field measurements in groundwater indicate that the inactivation of $\Phi X174$ may be minimal, even after several months (DeBorde et al., 1998).

Serratia Marcescens phage appears to be a robust tracer with long term viability being relatively unaffected by UV light and sorption. R_{90} times for removal of 90% of the viable phage in darkness range from 336 hours in River Water and 766 hours for Sea Water (Drury and Wheeler, 1982) suggesting an inactivation rate of around $0.03 - 0.07log_{10}$ per day. Wimpenny et al. (1972) indicate no decrease in Serratia Marcescens phage viability over the course of 1 week whilst Skilton and Wheeler (1989) indicate that Serratia Marcescens phage can survive in Chalk groundwater for at least a year.

Due to their colloidal nature, phage might be subject to both gravitational settling and size exclusion in the Chalk aquifer. Their size, which is comparative to that of chalk pore throats could restrict them from participating in matrix-fracture diffusion resulting in preferential transport in the fractures and conduit system. Bacteriophage may even be excluded from some micro-fractures in the Chalk.

5.2.1.2 Tracer Assay Method

Water samples were assayed for phage by CREH Analytical Ltd in accordance with the method detailed in: "The Microbiology of Recreational and Environmental Waters (2000), Methods for the Examination of Water and Associated Materials" (SCA, 2000).

The phage are assayed using a plate of suitable host bacterium which are directly infected with the phage sample, this leads to infection causing lysis of the bacterial host and the formation of plaques of dead bacteria. These plaques are then counted to provide a quantitative measurement of the number of viable phage in the sample. 1ml of groundwater sample is directly plated onto the host bacterium substrate. The concentrations obtained were therefore a direct reading of the number of phage per millilitre of water, this also forms the lower detection limit of 1 plaque forming unit per millilitre (pfu/ml). If a confluent lysis occurred (where the plaques overlap), the sample was diluted and re-tested until a measurement could be obtained.

Controls were carried out by the laboratory with every batch of samples to ensure that the host bacterium were not contaminated and that positive lysis could be obtained. Duplicate samples were not analysed, but the accuracy of a single count is considered to be ±20% of the true mean (Watkins, 2008, pers comm.).

For bacteriophage, the analysis method defines a count of the number of plaque forming units (pfu) (i.e. viable viruses) in 1ml of sampled water. The count provides a quantitative measurement and could broadly be considered to be equal to the tracer mass per unit volume, since the count is in discrete numerical units representing the number of phage which themselves are indivisible, i.e. a count of 1pfu/ml represents 1 active phage in that mililitre of water.

The detection limit of this method without any additional concentration is 1pfu/ml, although it is possible to concentrate samples in order to increase detection limits, this was not done as part of this investigation.

5.2.1.3 Tracer Risk Assessment

Bacteriophage tracers were selected for their non pathogenic nature, owing to their inability to replicate outside their bacterial host phage also have a limited lifespan within an aquifer environment and so will not persist or accumulate. A typical injection mass of around 10^{15} phage weighs only approximately 1g and hence tracer injection comprises an insignificant mass addition to the aquifer (Rossi et al., 1994). The Environment Agency considers that bacteriophage are of low overall risk and are not currently considered a biological tracer for which there is a priority for development of an Environmental Quality Standard (Whitehouse, 2001).

In accordance with United Kingdom best practice (Ward et al., 1998), and the requirements of the Environment Agency, a groundwater risk assessment for the tracers was undertaken to determine the maximum concentrations at nearby drinking water supply sources. Concentrations have been modelled using the equation presented in (Ward et al., 1998) based on Fickian one-dimensional dispersion (equation 5.1).

$$C_{MAX} = \frac{C_0}{A\sqrt{(4\pi r\alpha)}} \tag{5.1}$$

Where C_{MAX} is the maximum concentration at the receptor, C_0 is the injection concentration, A is the cross sectional area of the injection pulse, r is the distance to receptor and α is the coefficient of dispersivity.

The results of the risk assessment are presented in table 5.3. Despite the large numbers of plaque forming units anticipated, these predicted concentrations still

Table 5.3: Groundwater risk assessment for the bacteriophage tracers. *The subsurface depth of the swallow hole injection has been assumed from field data near North Mymms. The geometry of the water end swallow hole is assumed to be conical in form, giving a triangular cross sectional geometry. The tracer mass is assumed to spread to fill entire volume of solution void, ignoring the presence of infill material. **A value for α of 200m has been assumed in accordance with recent numerical modelling in the area Assem (2005).

Injection Location	Harefield House	Comet Way	Water End
Nearest Receptor	Nashes Farm	Hatfield Business Park	North Mymms PWS
Distance r (m)	460	974	982
Depth of borehole*	25.48	25	3
Well Diameter (m)	0.1	0.2	2
Saturated Thickness (m)	10.84	7.11	3
Area of Pulse A (m^2)	1.084	1.422	3
Dispersivity** α (m)**	200	200	200
Injected Mass M (pfu)	1×10^{16}	1×10^{16}	1×10^{16}
C_{MAX} (pfu/ml)	8.58×10^{6}	4.49×10^{6}	2.03×10^{6}

only equate to less than 1% of the total injected mass. Given the non pathogenic nature of the tracers selected, it was considered that tracing would not cause any environmental impact at the identified receptors. Furthermore, these calculations are conservation and ignore the affects of sorption and decay and the actual number of phage arriving at discharge points is likely to be lower than modelled.

5.2.1.4 Initial Tracer Titre

The tracers were received from the supplier, CREH Analytical Ltd on Friday 29th February 2008. Each tracer comprised a 1 litre solution of phage suspended in glycerol. To preserve the phage the solutions were placed in cold storage at $-20^{o}C$ for approximately 72 hours until the morning of Monday 3rd March 2008. The tracers were then removed and transported to the injection site in a cool box and were kept sealed until required for injection. The titration of each tracer as of 28th February 2008 is presented in Table 5.4

Table 5.4: Initial injection titres of tracer as at 28th February 2008

Injection Location	Phage	Titration (pfu/ml)	Total Number (pfu)
Harefield House	$MS2$	3.0×10^{13}	3.0×10^{16}
Comet Way	$\Phi X174$	4.0×10^{11}	4.0×10^{14}
Water End	*Serratia Marcescens*	3.0×10^{12}	3.0×10^{15}

5.3 Design of monitoring programme

Design of an effective sampling regime for tracer tests is challenging since it requires *a priori* knowledge or estimation of aquifer connectivity and likely travel times. Fortunately in Hertfordshire it is possible to constrain such assumptions based upon the conceptual understanding of the aquifer and, where available results from the

Table 5.5: Comparison of locations sampled for tracer from Water End during the 1930's tracer test (Harold, 1937) during the 1930's and in the present tracer test

Location	1920s/30s	2008
Amwell Hill PWS	√	×
Amwell Marsh PWS	√	√
Hoddesdon PWS	√	×
North Mymms PWS	√	√
Arkley Hole Spring	√	√
Chadwell Spring	√	√
Emma's Well Spring	√	×
Rye House Spring	√	×
Lynchmill Spring	√	√
Rye Common PWS	×	√
Turnford PWS	×	√
Hatfield PWS	×	√
New River at Amwell Marsh	×	√
Park Street OBH	×	√

previous tracer studies. Selection of sampling locations for the Water End injection was guided by locations previously sampled in the tracer testing during the early 20th century (Harold, 1937). A comparison of the locations sampled in the 1920's and 1930s and those sampled in 2008 is presented in Table 5.5

Nineteen locations were initially selected for sampling, and nearly all show elevated concentrations of bromate (except Coleman Green Lane OBH and North Mymms PWS) and are spatially distributed across the extent of bromate affected aquifer. All locations are currently sampled by the Environment Agency bromate monitoring programme or are major public supply abstractions. The distribution of sampling locations is shown in Figure 5.1 and a more detailed view of locations within the Vale of St. Albans in Figure 5.2

The exact sampling regime of the previous tracer test could not be fully replicated, since planned abstraction in TWUL's Northern New River (NNR) well field meant that during the time of the testing Hoddesdon PWS, Amwell Hill PWS were not in operation and could not be sampled. The spring-fed watercress beds at Rye House could no longer be located due to recent re-construction in the area, so as a substitute the presumed nearby TWUL pumping station at Rye Common was sampled as a proxy.

The spring at Emma's Well was observed prior to, and during the tracer test as being dry or having low flow. Whilst the spring could be observed from distance, direct access to the spring discharge point for sampling was not possible and the spring was not sampled during the investigations.

Additional locations, not previously sampled, at Broadmeads PWS and Broxbourne PWS were not in operation by TWUL and were not sampled during the period of the test. Turnford PWS was also not in operation, however, samples were collected by pumping for a short duration. Hatfield PWS, Essendon PWS, and the Park Street Observation Borehole in Hatfield were also monitored, the addition of these locations extends the area of observation to the west and further south

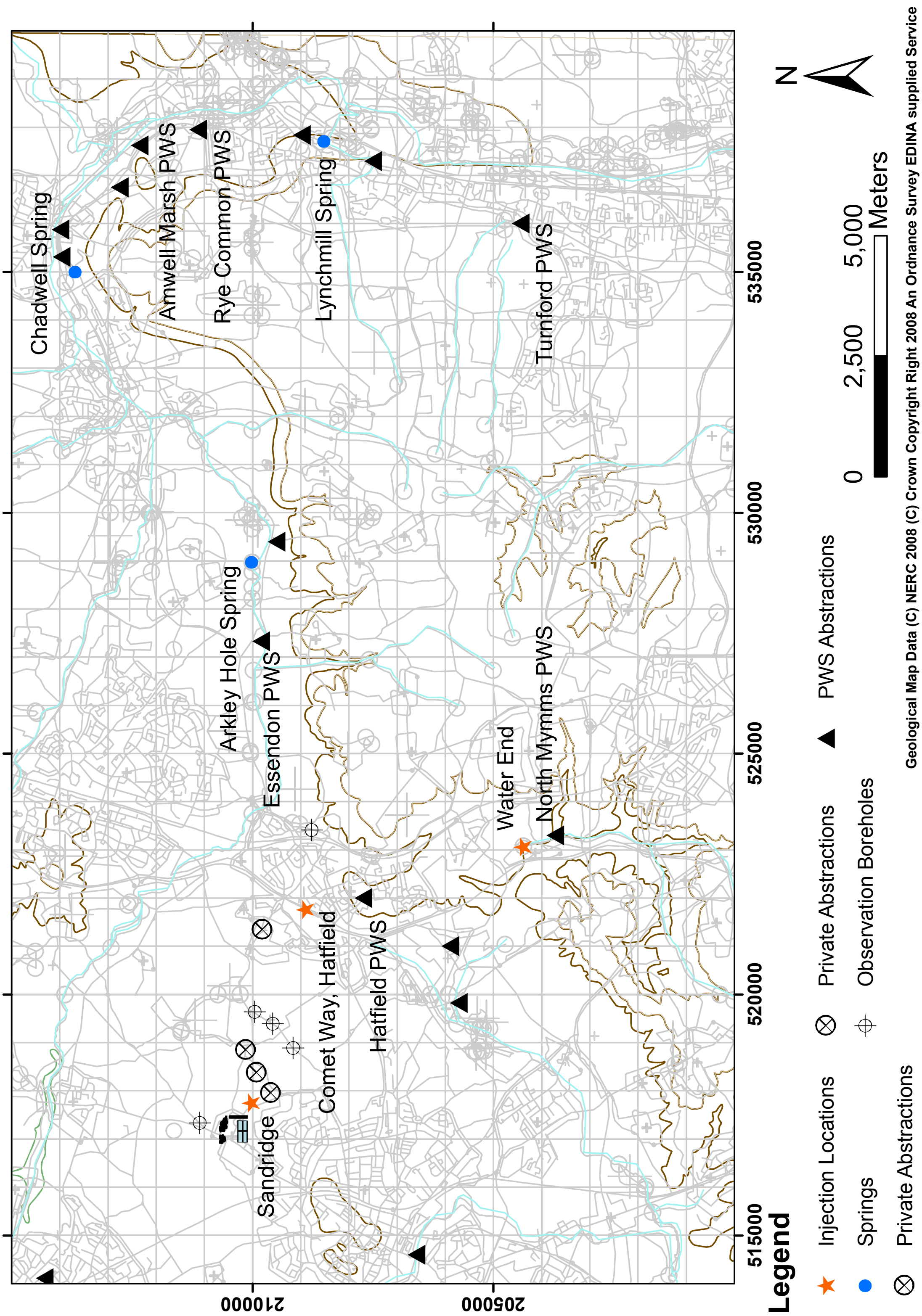


Figure 5.1: Tracer sampling locations

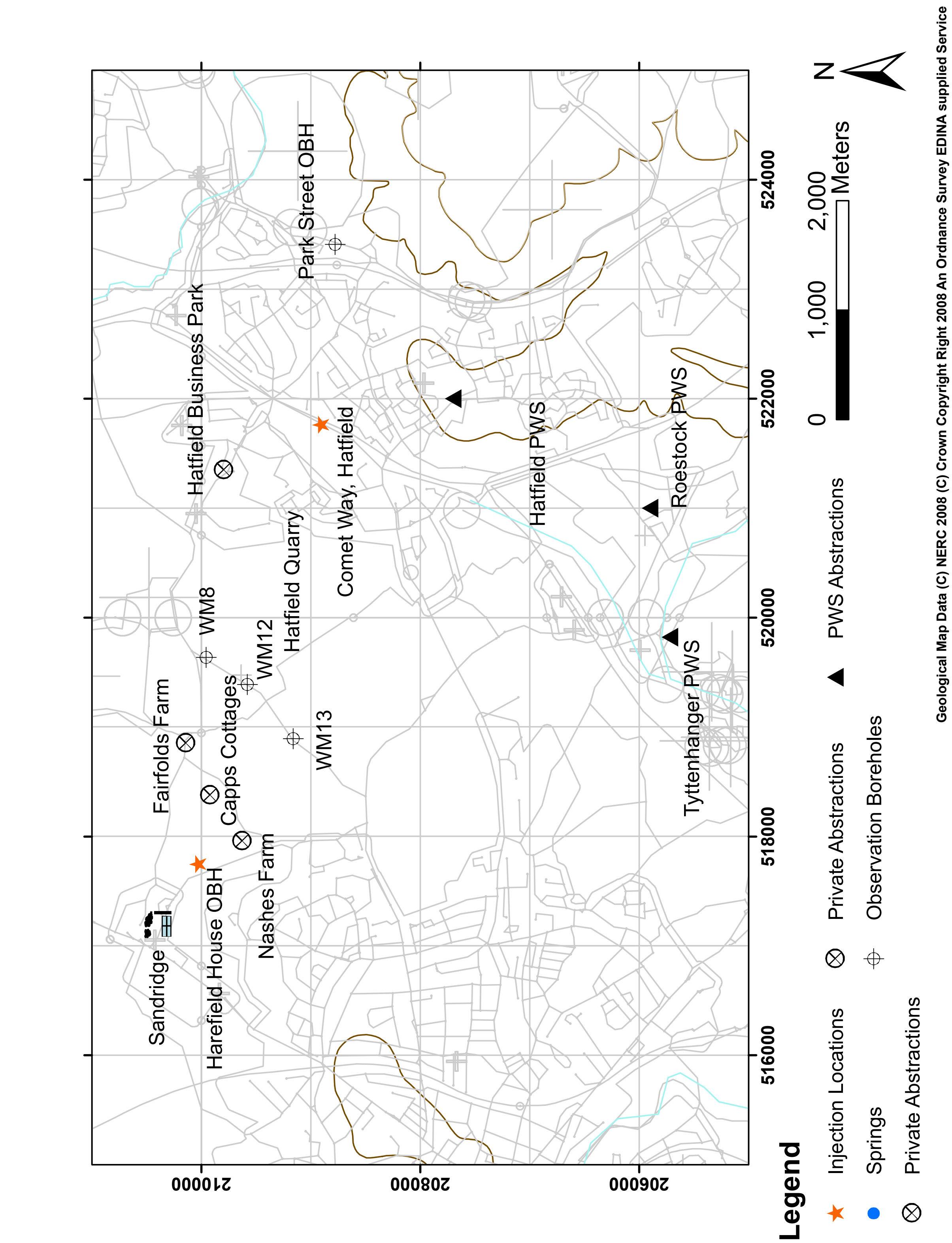


Figure 5.2: Tracer sampling locations within the Vale of St Albans

compared to that of Harold (1937). Quantitative analysis methods and a longer sampling duration also provide additional new information.

For the Comet Way (Hatfield) injection, sampling locations broadly mirrored those of the Water End injection since the aim was to establish the existence of karstic or semi karstic connections from the Hatfield Area. The observation borehole at Park Street was also monitored due to its position in a dry valley close to a set of Swallow Holes (at Howe Dell and Hatfield Park) and the Palaeocene Feather Edge.

For the Harefield House (Sandridge) injection, 8 Locations were monitored in the Vale of St Albans. These were distributed in two approximate NE-SW orientated cross sections across the bromate plume, comprising three private abstraction boreholes; Nashes Farm which was in regular use, Capps Cottage which was disused and Fairfolds Farm which was in regular use. Three shallow observation boreholes at Hatfield Quarry (WM8, WM12 and WM13) were also monitored.

Two further locations within or adjacent to the Vale of St Albans were sampled:

- An observation was monitored up-gradient of the injection point at Coleman Green Lane as both a background check and to determine if there was a flow-path
- An additional a private abstraction borehole located the Hatfield quarry site and Comet Way at Hatfield Business Park.

In addition to those sampling locations originally selected four additional locations were added during the tracer test:

- North Mymms PWS, added to allow comparison of the *Serratia Marcescens* Tracer at Water End with tests in the 1930's which indicated this location did not receive tracer from the swallow holes.
- The New River at Kings Mead, additional location added in the new river just downstream of it's diversion from the River Lee to monitor incoming tracer in the River System
- The New River at Emma's Well The New River at Emma's Well upstream to Amwell Marsh PWS to monitor bacteriophage concentrations in the New River
- The New River downstream of Amwell Marsh PWS to determine if the New River could used as a proxy for the pumping station in between sampling intervals.
- Sampling at low frequency was also conducted in the injection boreholes to monitor release of the tracer from the borehole.

Table 5.6: Parameter values adopted for use in the EHTD model (USEPA, 2003)

Parameter	Value adopted	Justification
Distance (m)		
Water End	8090	Based on grid references
Comet Way	7300	
Harefield House	11228	
Spring Discharge	4Ml/day	Atkins (2006)
Decay Constant	0.03	Collins et al. (2006)
Area of discharge point	12.56m^2	Estimate
Sinuosity Factor	1.2	Field and Nash (1997)

Table 5.7: Calculated sampling regime assuming karst conduit flow to Arkley Hole based on the EHTD model (USEPA, 2003)

Location Injection	Sample Interval (hours)	First sample (days)	Last Sample (days)
Harefield House	10	5	32.83
Comet Way	7	3.58	23.25
Water End	8	3.58	25

5.3.1 Sampling Frequency

The U.S. Environmental Protection Agency (USEPA) have developed the "Efficient Hydrologic Tracer-Test Design" (EHTD) methodology (Field, 2003). This model based approach was adopted to determine a first estimate of a sampling regime for the tracer test. The methodology is based on theoretical advection and dispersion of an injected tracer as an instantaneous pulse from the injection point to a discharging source. The methodology uses a computational programme to estimate tracer mass, sampling frequency and time to first sampling interval for both porous and karstic flow media. To obtain an initial estimate of a suitable sampling frequency a karstic flow case in the EHTD model was assumed between each injection location and Arkley Hole Spring since based on location this is likely to be the fastest confirmed connection based upon the tracer tests of Harold (1937). Table 5.6 shows the adopted parameters used in the EHTD model.

The sampling frequency and initial sampling times according to the EHTD model are presented in Table 5.7 below.

Although the EHTD sampling regime provides an indication of the frequency and timing of sampling it has several limitations and was therefore taken as a guide rather than adhered to rigorously. The karstic model in the EHTD assumes a direct tracer entry into a karstic conduit, in reality this is unlikely to be the case for borehole injections, although is probably reasonable for swallow holes.

The EHTD model does not envisage discharge to artificial sources such as boreholes or pumping wells since it is based on a single conduit model discharging to a spring, whilst this could be modified, discharge and cross sectional area of flow from conduits is not easily measurable in boreholes and hence the karstic model discharge has only been calculated for Arkley Hole, a known karstic spring using average discharge data from Atkins (2006).

The EHTD model is optimised to create a sampling regime containing approximately 65 samples since that is the minimum that the methodology considers appropriate to adequately define a tracer breakthrough curve. However, such a sampling regime is likely to be too onerous for achieving the principal objectives of this suite of testing; that of connectivity and travel time, hence first arrival and sampling times are more critical than sampling interval. Dual porosity diffusive exchange with the chalk matrix or micro fissures may also act to retard tracer arrival and lead to long tail times which are not accounted for in the tracer model. The transport model assumes a dissolved solute tracer rather than a bacteriophage suspended particulate tracer and in a number of cases bacteriophage tracers have been shown to have faster travel times than solute or dye tracers (e.g. Rossi et al., 1994; Taylor et al., 2004).

The modelled sampling frequencies also make no allowance for logistical considerations such as distance between sample locations, overall number of sampling locations or costs so in consideration of both the modelled sampling intervals were taken as a guide in combination with these more qualitative factors. The final sampling regime was designed in accordance with the following limitations:

- To aid sampling logistics, the minimum sampling interval at any given location was limited to daily unless automatic samplers were available.

- Initial EHTD sampling times have been used to determine start of sampling at sample locations.

- Since the principal aim of tracing is to establish travel times and connectivity based upon first or early arrivals the sampling frequencies are more frequently (daily) during the first two weeks of sampling, beyond this sampling frequency reduces by approximately half every two weeks.

- Sampling times for potential karstic flows have been derived from travel times inferred during previous karstic tracer studies (i.e. Harold, 1937) and the influence of scavenge pumping (Fitzpatrick, 2007).

- None of the locations has a sufficient sampling frequency in order to obtain the 65 recommended by the EHTD method

- Where possible, the sampling schedule attempted to sample locations that are geographically close on the same day and thus allow a cycle of sampling between locations spread across the assumed zone of tracer dispersion.

Since the sampled sites also comprised a range of very different locations including public supply wells, private wells, observation boreholes and springs the precise methodology adopted at each was slightly different and the method adopted at each and the nominal sampling frequency is detailed in Table 5.8

Table 5.8: Sampling details for all locations

Location	Sampling Method	Nominal Frequency	No. of Samples
Harefield House OBH	1l Bailer	Fortnightly	6
Comet Way OBH	1l Bailer	Fortnightly	5
Hatfield PWS	Sampled by TVW personnel	Daily	39
Essendon PWS	Sampled by TVW personnel	Daily 36	
North Mymms PWS	Sampled by TVW personnel	Daily	13
Amwell Marsh PWS	Sampled by TWUL personnel	3× Weekly	22
Rye Common PWS	Sampled by TWUL personnel	3× Weekly	6
Turnford PWS	Sampled by TWUL personnel	3× Weekly	21
Coleman Green Lane	Initially Sampled by pumping purging for 15mins. Later samples by 1l Bailer	2× Weekly	8
Nashes Farm	Initially sampled by 1l Bailer. Later sampled from in hole pump, no purging	2× weekly to weekly	13
Capps Cottages	Sampled by 1l Bailer	2× Weekly to Weekly	13
Fairfolds Farm	Sampled from in hole pump feeding water tank	2× Weekly to Weekly	12
Hatfield Quarry WM8	1l Waterra Bailer. Between 6 and 15l of water removed prior to sampling	2× Weekly to Weekly	11
Hatfield Quarry WM12	Sampled by 1l Waterra Bailer. Between 6 and 15l of water removed prior to sampling	2× Weekly to Weekly	11
Hatfield Quarry WM13	Sampled by 1l Waterra Bailer. Between 6 and 15l of water removed prior to sampling	2× Weekly to Weekly	11
Hatfield Business Park	Sample from raw water tap via pump, no purging	2× Weekly to Weekly	4
Park Street OBH	Initially Sampled by pumping, purging for 15mins. Later samples by 1l Waterra Bailer	2× Weekly to Weekly	9
Arkley Hole Spring	Auto-sampler (figure 5.3)	12 Hourly	106
Lynchmill Spring	Auto-sampler (figure 5.4)	12 Hourly	125
Chadwell Spring	Manually sampled by filling bottle from spring discharge pool	Daily to Weekly	18
Kings Mead (New River)	directly from New River	Weekly	7
Emma's Well (New River)	directly from New River	Weekly	7
Amwell Marsh (New River)	directly from New River	Weekly	10
Total Number of Samples		513	

The general sampling procedure followed is described below:

1. Prior to sampling the standing water level in the borehole or spring discharge/stage was recorded.

2. Purge borehole/well if required (see Table 5.8).

3. Samples of around 100ml were collected in a sterile amber glass bottle leaving a small amount of air space.

4. Sample bottle filled leaving some air space then seal.

5. Dry exterior of sample bottle with a clean tissue.

6. Samples were labeled with the 3 digit EA database location (see Hay and Buckle (2006)) followed by 8 digits comprising the date of sampling in the format DDMM and the time in the format HHMM using the 24 hour clock to ensure a unique traceable number for each sample and reduce the risk of mislabeling, e.g. a sample collected at Hatfield PWS on 2nd of March at 13:15 would be labeled 001/0203/1315.

7. The time, date and location of the sample were also recorded in words on both the sample bottle and sample record sheet.

8. Since the primary causes of bacteriophage inactivation following sampling are exposure to UV light and to temperatures above 20^oC. To limit exposure to UV, sample bottles were sterile brown amber glass.

9. Collected samples were refrigerated or kept in a cool box and stored in the dark after collection and dispatched for analysis as soon as possible.

5.3.1.1 Steps Taken to Reduce Cross Contamination

To reduce the risk of cross contamination of samples between monitoring locations, the following steps were taken:

- Tracers and all associated injection equipment were transferred to site separately from the sampling vehicle and all injection equipment was bagged sealed and removed from site

- New changes of clothes were worn on site each day and between each injection location on the day of injection - Samples of 100ml were collected in sterile amber glass bottles in order to reduce sorption to the bottle and protect them from UV light exposure.

- Sterile latex gloves were worn at all times whilst handling samples and were changed between each sample site and at locations of auto-samples

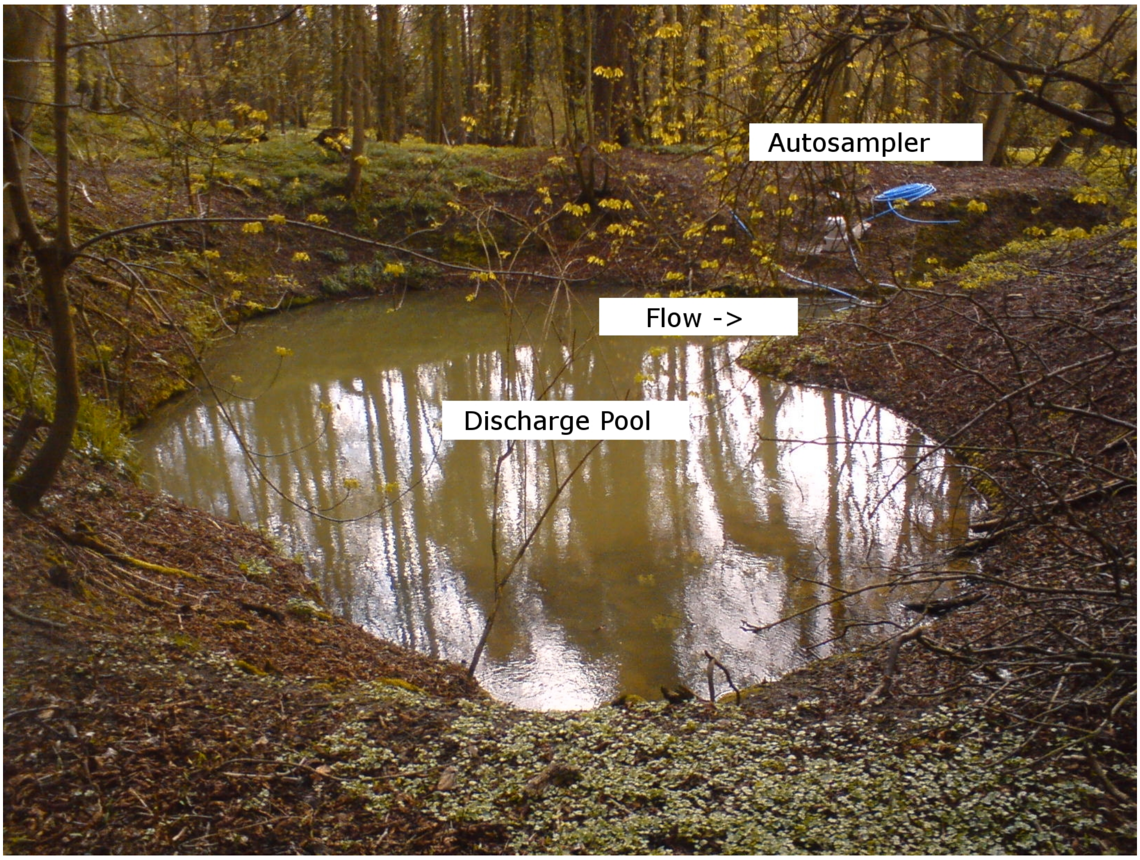


Figure 5.3: Position of Automatic Sampler at the exit of the Arkley Hole Spring discharge pool

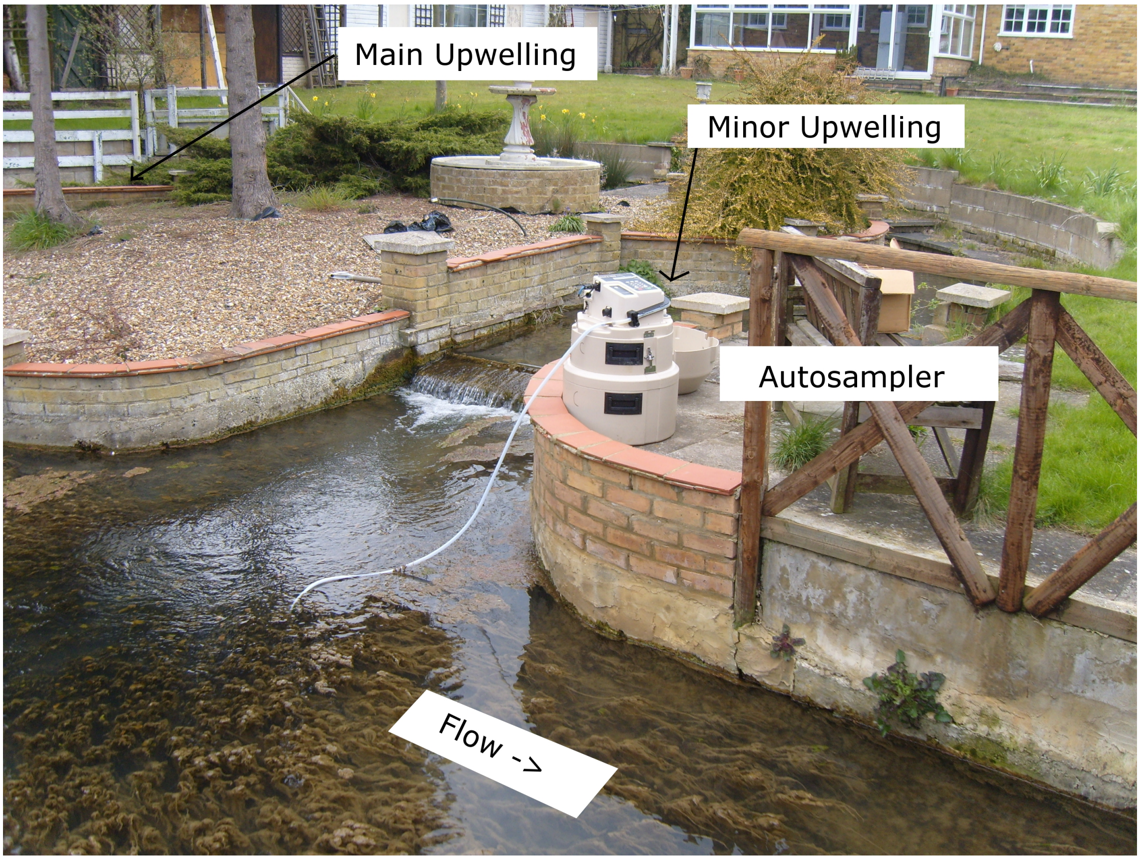


Figure 5.4: Position of Automatic Sampler at the confluence of the discharge channels from the two outlets at Lynchmill Spring

- Samples were bagged, sealed and placed in a dark lined cool box at $\approx 10^oC$ immediately after sampling and placed in a refrigerator within a few hours of collection in order to reduce inactivation.
- Sampling equipment such as auto-sample bottles, borehole bailers and buckets were sterilised between use with boiling water and a dilute hypochlorite solution
- Auto-sampler intake tubes had three pre-rinse and flush cycles programmed prior to, and following collection of each sample to ensure that a fresh sample was collected
- Sampling of PWS sites was undertaken by TVW and TWUL personnel who had no contact with the tracer injection
- Most samples were dispatched within 24 hours of collection for analysis and most analyses were complete within 48 hours

5.3.1.2 Limitations of the sampling methodology

The sampling interval places a limit on the accuracy with which tracer breakthrough travel times and peak concentrations can be interpreted between the timing of the first measurable detection and the previous sample which did not contain detectable levels of Bacteriophage. It is also impossible to know if the apparent peak concentration that was sampled reflects the actual peak concentration since due to the transient nature of breakthrough it is unlikely that sampling took place during peak concentrations.

5.4 Results of Background Sampling

Prior to injection of the tracers an irregular programme of background sampling was undertaken. The background sampling was aimed to provide quantitative information about the background presence and variability of the Bacteriophage tracers in the groundwater of the study area. In addition, the background sampling was originally meant to inform the selection of Bacteriophage species to be used as tracers. However, owing to the long lead time required by the tracer supplier to prepare the tracer doses (between 6 and 8 weeks) and other logistical constraints, it was not possible to obtain any samples prior to ordering the tracer species.

Tracer selection was also constrained by the supplier, whom could only provide four bacteriophage species; $MS2$, $\Phi X174$, *Serratia Marcescens* and a species of Enterobacter phage. A review of available literature for Bacteriophage as groundwater tracers led to the selection of $MS2$, $\Phi X174$ and *Serratia Marcescens* species as these had successfully been used in previous groundwater tracer tests (e.g. Skilton

Table 5.9: Results and summary statistics for the background sampling, likely upper estimates based on 2 and 3 standard deviations from the mean and assuming a normal distribution have been rounded to the nearest integer to account for the discrete nature of phage

Location	Date	Phage Concentration (pfu/ml)		
		$MS2$	$\Phi X174$	*Serratia Marcescens*
Arkley Hole Spring	05/02/2008	5	3	0
Arkley Hole Spring	27/02/2008	0	0	1
Capps Cottage	28/01/2008	1	0	-
Capps Cottage	25/02/2008	1	-	-
Chadwell Spring	08/02/2008	2	1	0
Chadwell Spring	27/02/2008	0	0	0
Coleman Green Lane OBH	25/02/2008	0	-	-
Essendon PWS	05/02/2008	1	3	0
Essendon PWS	26/02/2008	0	0	0
Fairfolds Farm	28/01/2008	1	0	-
Fairfolds Farm	25/02/2008	0	-	-
Harefield House	25/01/2008	2	0	-
Hatfield PWS	05/02/2008	1	0	0
Hatfield PWS	26/02/2008	0	0	0
Hatfield Quarry WM12	25/02/2008	0	-	-
Hatfield Quarry WM13	25/02/2008	1	-	-
Hatfield Quarry WM8	25/02/2008	0	-	-
Lynchmill Spring	08/02/2008	5	4	1
Lynchmill Spring	27/02/2008	2	0	0
Park Street OBH	25/01/2008	-	0	0
Park Street OBH	25/02/2008	0	0	0
Total		20	15	12
Positives		10	4	2
Minimum		0	0	0
Mode		0	0	0
Mean (μ)		1.1	0.73	0.17
Maximum		5	4	1
Standard Deviation (σ)		1.52	1.39	0.39
$\mu + 2\sigma$ (95%)		4	4	1
$\mu + 3\sigma$ (99%)		6	5	1

and Wheeler, 1989; Price et al., 1992) in the Chalk aquifer and some data were available regarding transport and inactivation rates (see Section 5.2.1.1).

Background sampling was undertaken in January and February 2008. A total of 22 samples from 14 locations were collected. Of these samples, 16 were analysed for $MS2$, 11 were analysed for $\Phi X174$ and 8 were analysed for *Serratia Marcescens*. The locations of the background samples are indicated in Figure 5.1 and the results are presented in Table 5.9

Background analyses for $MS2$ bacteriophage showed variation in concentrations ranging from 0pfu/ml to 5pfu/ml. The two highest background counts, both of 5pfu/ml, are in single analyses from the two spring discharges at Arkley Hole and Lynchmill Spring, however all locations sampled/analysed on more than one occasion show a background of at least 1pfu/ml of MS2 bacteriophage. No strong spatial variation is easily discernible. The background data suggest the possibility that a concentration of 1pfu/ml MS2 Bacteriophage is relatively common and should be expected and that less frequent higher counts (> 2) may occur where there is a

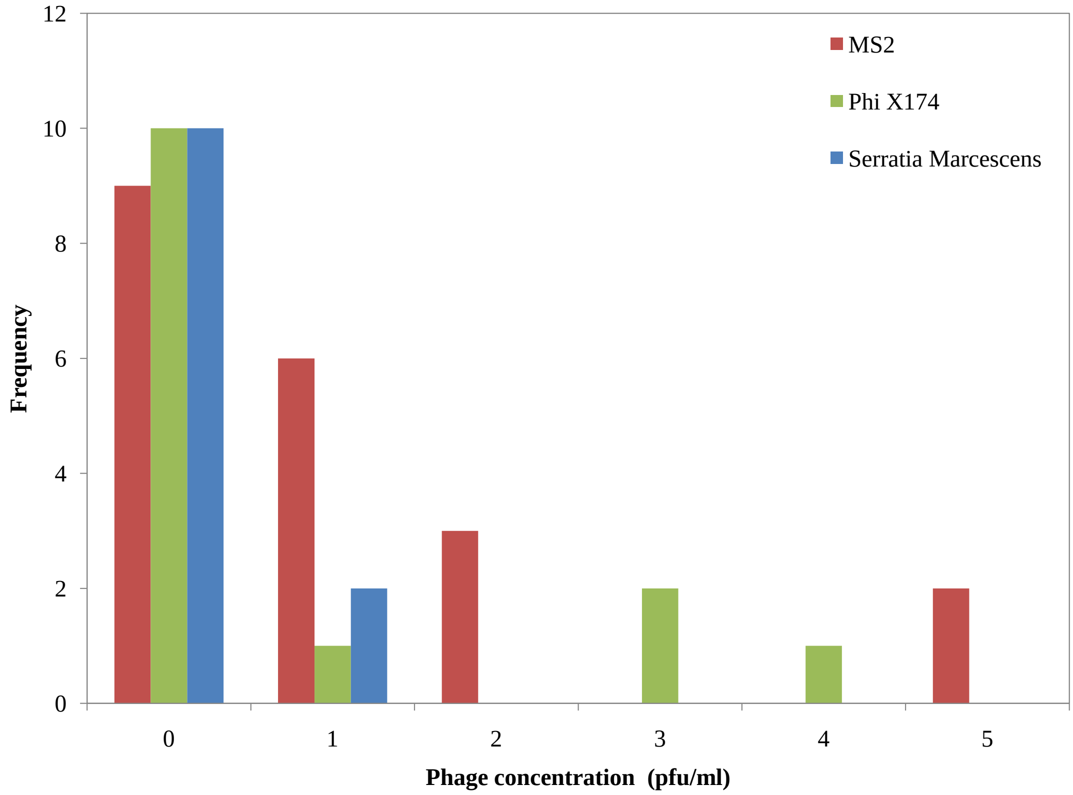


Figure 5.5: Histogram showing the frequency and concentration of background samples for the three phage species

karstic component to the groundwater discharge.

Background analyses for $\Phi X174$ phage (on 11 No. Samples) showed variation in concentration from 0pfu/ml to 4pfu/ml. The highest background concentration of 4pfu/ml is in a single analyses from the spring discharge at Lynchmill Spring. Of the 9 Locations sampled for $\Phi X174$ positive background concentrations were only detected at Lynchmill Spring, Arkley Hole, Chadwell Spring and Essendon PWS, all locations which are considered to have a strong karstic component to discharge but it should be noted that only 2 samples were collected from locations within the vale of St Albans, the rest were all located close to known karstic features or within 200m of the Palaeocene outcrop and therefore there may be some inherent location bias to this conclusion.

Background analyses for *Serratia Marcescens* phage (on 8 No. Samples) showed less variation in Bacteriophage concentrations than the other phage ranging from 0pfu/ml to 1pfu/ml. Only two samples tested positive for *Serratia Marcescens* phage both indicating a concentration of 1pfu/ml. The two positive detections occurred at the two spring discharges at Arkley Hole and Lynchmill Spring.

To investigate if the background concentrations can be approximated by a normal distribution they have been plotted on a normal probability plot (Figure 5.6. Comparing the r^2 values to critical values of the normal probability plot correlation coefficient suggest that they are normally distributed at the 5% significance level and a normal distribution can be assigned to the data.

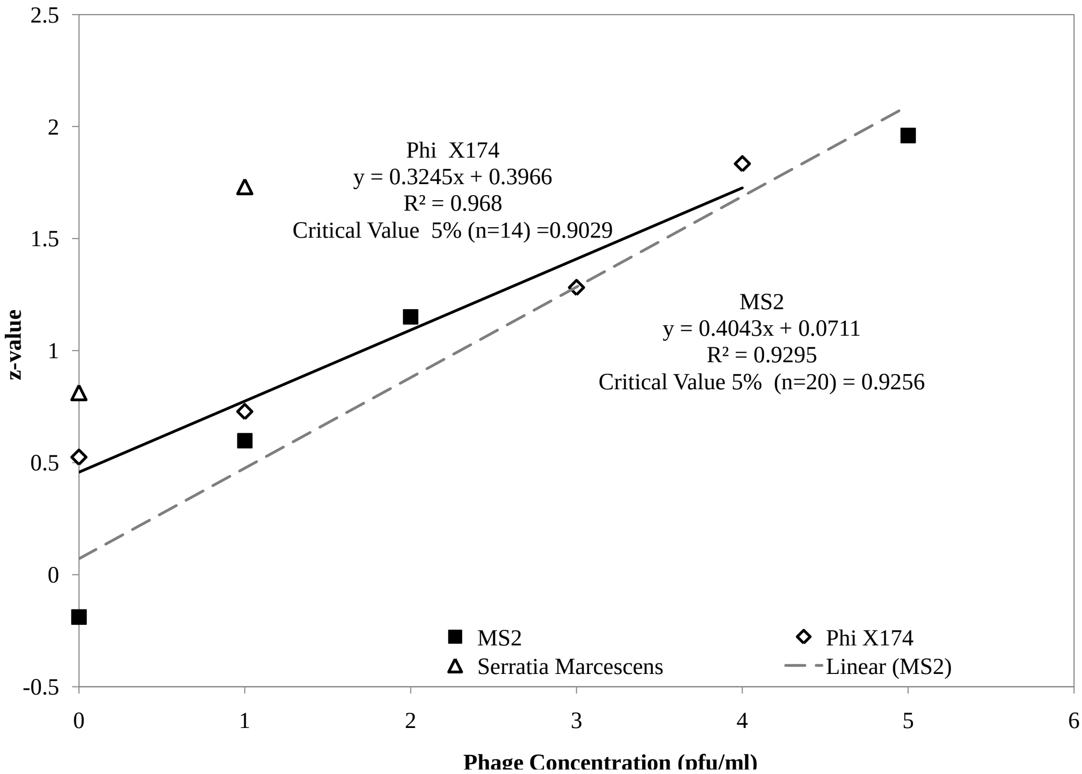


Figure 5.6: Normal probability plot for the background sampling. The data approximately follow normal distributions at the 5% significance level

From the data available, the following general trends in the background occurrence of Bacteriophage species can be determined:

- All background concentrations are less than 5pfu/ml and appear to be normally distributed.

- The statistical distribution of the data suggest that approximately 1 in 22 of MS2 and $\Phi X174$ samples will have a background concentration in excess of 4pfu/ml and 1 in 370 with a background concentration in excess of 5 or 6pfu/ml $\Phi X174$ and $MS2$ respectively.

- The natural background of *Serratia Marcescens* is expected to be $\leq$ 1pfu/ml.

- $MS2$ phage occur commonly, probably a background level of 1pfu/ml can be expected with less frequent higher concentrations

- Background occurrences of $MS2$ phage occur more frequently than $\Phi X174$, however when detected $\Phi X174$ show slightly higher concentrations. Both species occur more frequently and at higher concentrations than *Serratia Marcescens*.

- Spring/Karstic Locations tend to show higher background concentrations than borehole discharges.

- The highest concentrations of $MS2$ coincide with the highest concentrations of $\Phi X174$ which might suggest a common origin.
- The background samples indicate that *Serratia Marcescens* would be the most sensitive tracer since it has the lowest background frequency and concentrations. This is especially true in karstic discharges such as Arkley Hole and Lynchmill Spring where higher background of the $MS2$ and $\Phi X174$ phage may make detection of breakthrough more difficult.
- MS2 is present at background levels throughout the aquifer and the range of the background appears to be relatively consistent although may be higher in karst spring discharges. MS2 also has a much higher injection titration than other species so it was considered that breakthroughs might be more easily distinguished from the As a result MS2 was injected into what was considered to be the dominantly fracture flow/dual porosity dominated area of the aquifer close to the Bromate source at Harefield House.

5.4.1 Possible origins of the background

Bacteriophage are present in a wide range of environments such as water, soils sewage, wastewaters and sediments. They occur in-frequently in human and animal faeces and are common in waste water discharges. Coliphage, particularly male specific phage such as $MS2$ are present in human waste waters, but not human faeces (Havelaar et al., 1986). Wastewaters could include septic tank effluent (Jin et al., 2000) and phage may also be present in other sources of waste water such as agricultural muck spreading or discharges from waster water treatment works. This could provide a potential source of the phage in surface waters via rainfall and run-off.

These and possibly other sources of phage, such as leaking sewers, could reach groundwater via recharge and percolation through the un-saturated zone, although this can be fairly large in Chalk and hence phage may be subject to a degree of sorption or inactivation (Jin et al., 2000). Studies of this sorption typically only detect sporadic occurrences of enteroviruses in groundwater beneath wastewater sites, usually these relatively close to the discharge point suggesting that sorption might be important although this appears to be dependent upon the depth and absorptive capacity of the soil (Funderberg et al., 1981).

Sources of water which may bypass the unsaturated zone fairly rapidly such as flow through swallow holes might be subject to less sorption and as a result background phage concentrations may vary with discharge to swallow holes, and other parameters such as rainfall and turbidity, as has been shown for bacterial counts in ground following discharge to the Water End swallow holes (Harold, 1937).

5.4.1.1 Turbidity and Rainfall

Rainfall during the tracer test might provide a source of additional tracer free water to the aquifer via recharge. This could either be via diffuse recharge where rainfall falls on the Chalk outcrop, surface run off to streams and swallow holes or surface run-off to the River Lee and New River as well as spring discharge pools which would act as diluting the measured concentrations of phage tracer. Surface run-off might also pick up bacteria and organic matter and this could include either phage host species or the phage themselves and could serve to be a potential source of the measured background.

Rainfall increases the bacterial count and turbidity of water at at a number of locations and has been linked to increased surface run-off entering the Swallow Holes at Water End and elsewhere (Harold, 1937). This provides a mechanism by which phage host bacteria and phage themselves may enter the aquifer via swallow holes at Water End and elsewhere.

Daily precipitation data for the London (NGR 5310 1819) and Andrewsfield (NGR 5687 2247) weather stations were provided by the Met Office for the duration of the tracer test, these data are presented in Figure 5.7. Both locations follow the same general pattern but Andrewsfield has a slightly greater amount of rain. The following periods of rainfall are of note:

- Rainfall was negligible during the injection period up until the 8th March
- Over 20mm of rain fell in the region between the 8th and 10th of March 2008
- A further 20mm+ of rain fell in the region between the 13th and 16th of March, 2008 following this, a relatively dry spell lasted until the 20th
- Several smaller rainfall events are then recorded typically between 4 and 8mm per day separated by relatively dry spells.
- Heavy rain, totalling up to 30mm occurred towards the end of the sampling regime between April 27th and 30th.
- Total rainfall over the period was 119mm at London and 152.2mm at Andrewsfield

Turbidity data for Essendon PWS have been supplied by TVW for the duration of the Tracer testing. Turbidity at Essendon is known to increase following rainfall events and occasionally during high turbidity periods, abstraction at Essendon is temporarily suspended. Prior to this series of tracer tests this was inferred to be due to connection to the Water End Karst system, the increased turbidity due to surface run-off entering from the swallow holes following rainfall. Since bacterial counts are also known to increase at locations receiving water end discharge following rainfall (Harold, 1937) Turbidity could be considered as a proxy for bacterial presence in

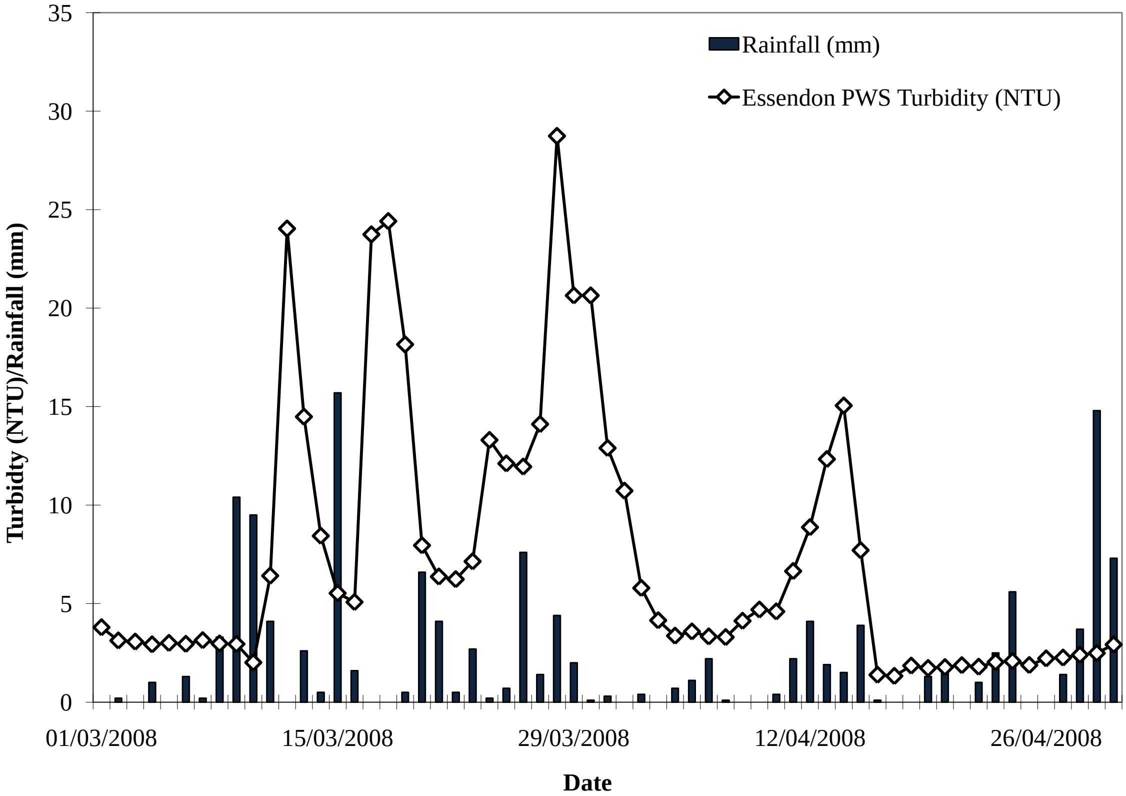


Figure 5.7: Averaged daily rainfall at Andrewsfield and London weather stations and the variation in groundwater turbidity at Essendon PWS

the borehole and therefore might indicate periods during which background concentrations of phage might also be relatively high. Figure 5.7 indicates the variation in measured turbidity in the raw water discharge at Essendon PWS for March and April 2008, as well as the average rainfall between London and Andrewsfield.

Turbidity appears to increase following rainfall events although there is a lag of between 2 and 3 days following peak daily rainfall and peaks of measured turbidity, probably representing the time for run-off and recharge to enter the groundwater and travel to discharge locations. Qualitative observations made during the tracer test sampling indicated that turbidity at both Arkley Hole and Lynchmill Spring sites was observed to increase following rainfall and clear over a period of 3-5 days.

5.5 Tracer Injection

5.5.1 Boreholes

In accordance with guidance received from the tracer supplier (Watkins, 2008, pers.communication) the tracer solutions required dilution in order to reduce the viscosity and density of the glycerol suspension in which they were delivered, relative to the groundwater and better enable migration of the tracer.

Single Borehole Dilution Tracer testing (SBDTT) (Fitzpatrick, 2008) conducted at both injection boreholes was used to guide the tracer injection depth to active

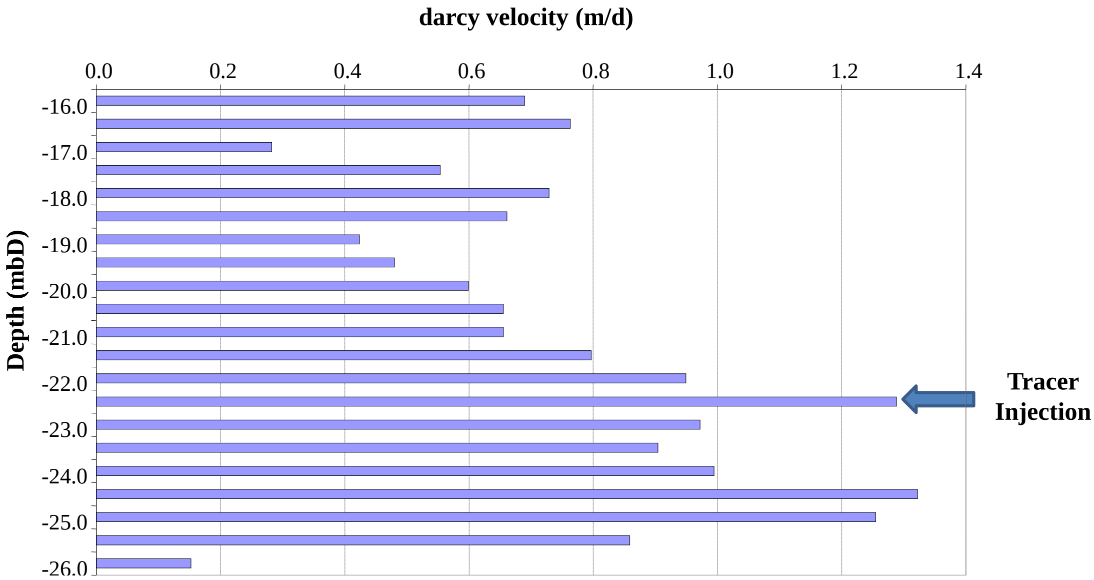


Figure 5.8: Results of single borehole dilution tracer testing at the Harefield House tracer injection borehole (Fitzpatrick, 2010). The depth of tracer injection is illustrated at 22m below borehole datum.

flow horizons. The method for injection was the same as that previously used by (Skilton and Wheeler, 1988).

- For each of the injection boreholes 20L of groundwater water was abstracted, of this 10L was mixed with the 1L injection glycerol suspension of tracer to create 11L of tracer suspension.

- A 10mm diameter hose cut to the required length and weighted at the base was used to inject the tracer to the required depth, tracer was injected by pouring into the hose via a funnel. The additional 10L of groundwater extracted prior to injection was then used to flush the injection hose and provide an additional driving head for the tracer into the boreholes.

5.5.1.1 Harefield House

The Single borehole Dilution Tracer Test (SBDTT) at Harefield house (Fitzpatrick, 2008) (See Figure 5.8) indicates velocities from 0.15 – 1.3m/day. The highest flux occurs in the lower part of the borehole between 21.5 and 25.5mbD. The bacteriophage were injected at an active flow horizon at 22.5mbD. The 11l of dilute tracer solution was added to the injection hose in $\approx$ 0.75l doses between 12:07 and 12:20 pm on March 1st. The hose was then flushed with 10l of groundwater from 12:20 to 12:24.

Figure 5.9: Mixing and Injection of Coliphage $MS2$ Coliphage Tracer at the Harefield House Observation borehole, Sandridge 03/03/08

5.5.1.2 Comet Way

The SBDTT at Comet Way indicated rapid dilution of the sodium chloride tracer within the borehole, with the electrical conductivity returning to background levels in under 3 hours. Geophysical Logging (Randle, 2008) indicated a slight downward flow within the borehole below 17m below datum (top of casing). The SBDT profile indicated flows were faster than at Harefield house (Figure 5.10). The tracer was injected at 18m below datum. This was close to the mid point of the Water Column between the base of the plain casing at 16.9mbD and the plumbed depth of the borehole at 19.6mbD. Tracer was added to the injection hose in $\approx$ 0.5l increments from 10:45 until 10:55. The hose was then flushed with a further 10l of groundwater.

5.5.2 Water End Swallow Holes

At Water End, the point at which the Mymmshall Brook sinks into the swallow holes of the complex could not be reached safely on foot due to overgrown vegetation and the uneven and unstable terrain. The lower swallow holes at the northern end of the complex were not active indicating that the entirety of the stream water was entering the ground somewhere between the Mymmshall Brook entry point and the northern end of the complex. The tracer was released directly into the Mymmshall Brook at the closest point upstream of the swallow holes that was easily accessible safely on foot at NGR TL 230 039, the location of which is indicated in Figure 5.12 approximately 320m upstream of the first swallow hole in the complex. 10l of Stream

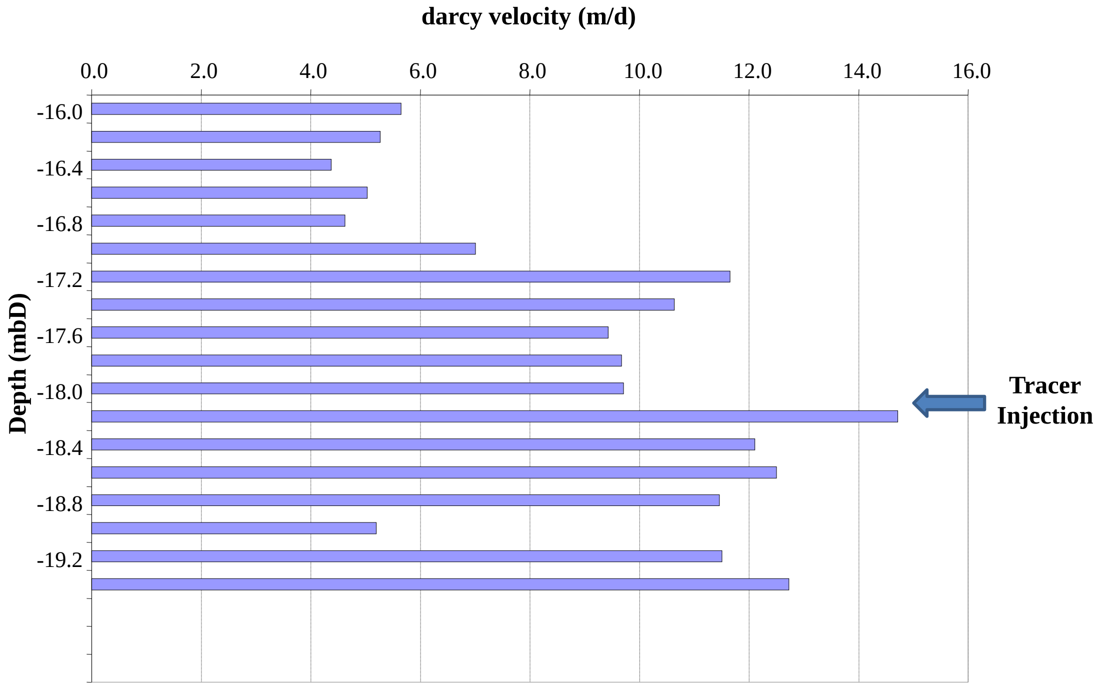


Figure 5.10: Results of single borehole dilution tracer testing at the Comet Way tracer injection borehole (Fitzpatrick, 2010). The depth of tracer injection is illustrated at 18m below borehole datum.

Figure 5.11: Mixing and Injection of $\Phi X174$ phage tracer at the Comet Way Observation borehole, Hatfield 03/03/08

water was extracted from the Mymmshall Brook at the injection location and mixed with the 1l suspension of 3×10^{12}pfu/ml of *Serratia Marcescens* bacteriophage. The solution was poured into the Mymmshall Brook at 14:00.

No sampling of the tracer progression down stream towards the swallow holes could be undertaken. It is likely that some dispersion and dilution of the tracer suspension occurred between the injection point and the swallow holes, it is also possible that some of the tracer might have become inactive, sorbed to river material or trapped in stagnant zones of the river. Swallow holes, which are known to occur in the Mymmshall Brook upstream of the injection point may also be present between the injection point and the main Water End complex and it is possible that they may also have adsorbed some proportion of the tracer.

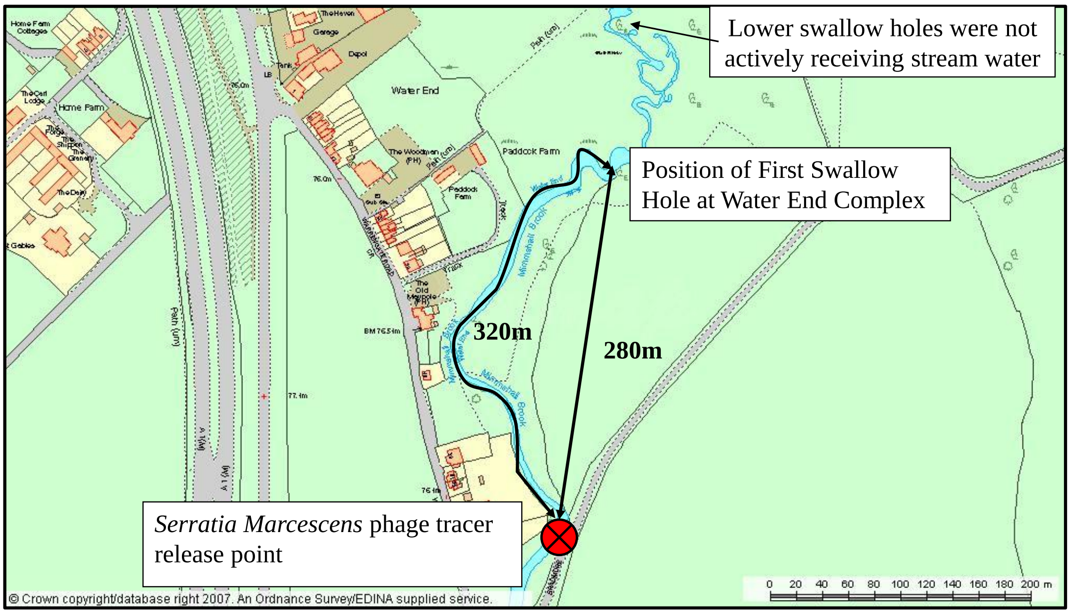
5.6 Sampling at Injection Boreholes

To minimise the risk of cross contamination it was initially intended that following injection, all sampling and injection equipment would be removed from, and not returned to site. It was intended that the tracer injection boreholes would not be re-visited or sampled during the test in order to minimise risk of cross contamination but planning did allow for the sampling of the injection boreholes if no detection of tracer species had been made after the first two weeks of sampling. Detection of *Serratia Marcescens* phage at levels in excess of the background range ($0-1pfu/ml$) had occurred within the first 10 days of sampling, it was not considered necessary to return to the Mymmshall Brook to sample the stream water.

Assessment of the available data for $\Phi X174$ and $MS2$ phage (see Sections 5.10.3 and 5.9) as of 13th March 2008 indicated that only two samples showed $\Phi X174$ and $MS2$ phage counts above that of the background range. Results for these phage were also inconsistent with what might have been expected had a pulse of tracer been migrating to these locations since they were dominantly sporadic results within the natural background range and the majority of analyses indicated phage concentrations counts of 0pfu./ml.

To assess the migration of tracer from the injection boreholes, 6 Samples were collected and analysed from the Harefield House OBH ($MS2$) and 5 samples were collected and analysed from the Comet Way OBH ($\Phi X174$). To minimise the risk of cross contamination they were sampled at the end of that days sample round and all equipment and clothing used was bagged, sealed, then removed from and not returned to site for the remainder of the tracer test. The results from the sampling are presented in table 5.10.

Water levels were not measured in order to prevent contamination of the borehole dipper. If it is assumed that the injection boreholes had the same saturated volume as during injection (21.9l at Harefield House and 63.4l at Comet Way) and it is also



(a) Position of the release point for the *Serratia Marcescens* tracer upstream of the main swallow hole complex

(b) Release of the tracer into the Mymmshall Brook at 14:00 on 03/03/08

Figure 5.12: Release of the *Serratia Marcescens* tracer

assumed that the samples were representative of the numbers of phage throughout the borehole (i.e. the borehole mass had been evenly mixed) these data would suggest borehole waters would have a total number of 2.19×10^{10}pfu $MS2$ phage at Harefield house and 8.25×10^{11}pfu $\Phi X174$ phage at Comet Way. Comparing these counts to the initial titration of phage indicates that of the original injection dose, less than 1% of the total bacteriophage injected were present in either injection borehole.

The assumption of even mixing of tracer within the injection boreholes by these calculations is incorrect and the calculations probably overestimate the tracer concentration remaining since the injections were designed to place the a limited volume phage at a specific depth. These data also indicate that even mixing was probably never achieved, since if the initial injection dose had been evenly distributed through the entire saturated volume (including the injection and flushing volume) it would result in an overall concentration in the borehole of 1.37×10^6pfu/ml $MS2$ at Harefield House and 4.85×10^2pfu/ml $\Phi X174$ at Comet Way, concentrations much lower than that determined in the analyses.

If it is assumed that no mixing with borehole waters had occurred due to stagnant flow within the borehole which is again probably unrealistic, and the phage concentrations relate purely to sampling the proportion of the borehole that represented the original injection volume ($\approx$ 21l in total) then the total phage number within that volume as of the 15th March 2008 would be 2.01×10^{10}pfu $MS2$ at Harefield House and 2.73×10^{11}pfu $\Phi X174$ at Comet Way. However, this still accounts for less than 0.0005% of the total $MS2$ phage injected and 0.01% of the total $\Phi X174$ phage injected.

These data indicate that a large proportion of tracer mass had either left the borehole or became inactive in the first 12 days following injection, this is consistent with investigations of phage survival in groundwater (e.g Cronin and Pedley, 2002) who reported a high initial inactivation followed by a relatively slow decay.

5.6.1 Remobilisation of Borehole Tracers

In order to increase the mobility of the tracer remaining in the borehole and maximise mass released to the aquifer the tracer remaining within the boreholes was "re-mobilised" on 31st March 2008. The procedure employed was the same at both injection boreholes: The boreholes were bailed from the base of the water column using a 1L disposable bailer which was removed to the surface and then poured back down the borehole so as to effectively mix the water column. This was repeated until a volume of water had been removed and re-poured equal to approximately half the volume of the water column. This volume was determined from approximate estimates of the groundwater level based upon previous dip measurements and was not measured at the time to prevent cross contamination. Figure 5.14 provides a

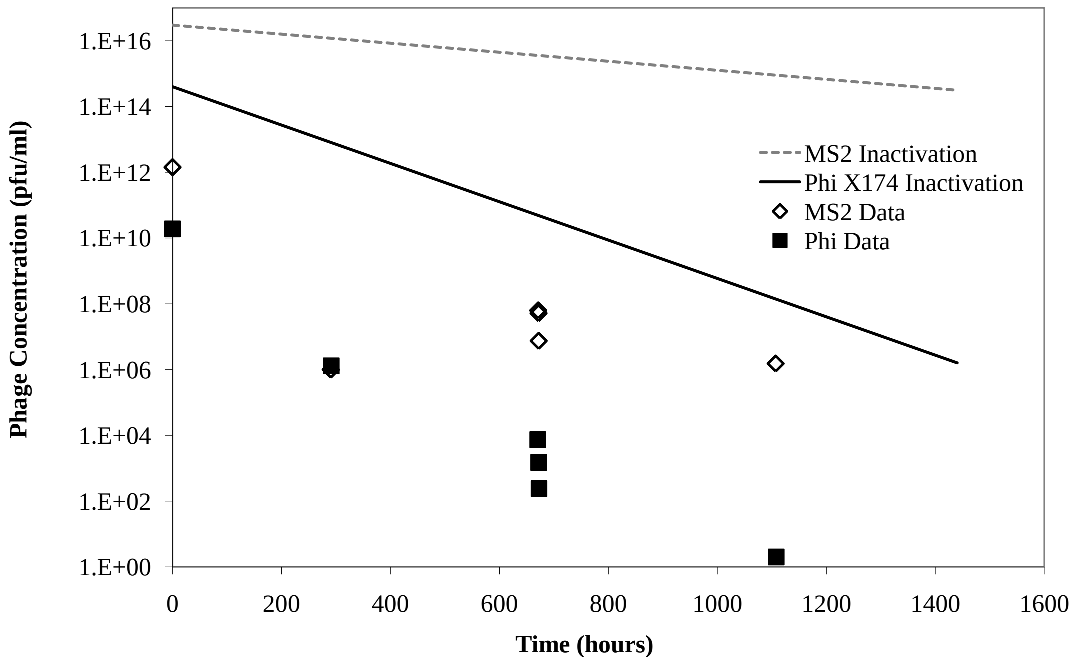


Figure 5.13: Variation in injection borehole concentration with time. The loss of tracer from the borehole follows a log-linear relationship reflecting both inactivation and flux from the borehole, the remobilisation accounts for the step in concentrations at approximately 680 hours

schematic description of the remobilisation procedure.

The overturning of the boreholes would not have been perfect since the bailer allows through-flow and mixing within the bailer volume as they are raised and lowered. The mechanical action caused by the bailer movement in combination with the extraction and re-pouring would probably be sufficient to mix the water column. Samples were taken for phage count analysis at the start and end of the re-mobilisation procedure and then again after approximately 2 hours had elapsed in order to monitor the effectiveness of the remobilisation.

Prior to the start of the remobilisation, tracer concentrations at Comet Way were lower than when previously sampled on March 10th indicating further decay or migration of the tracer had occurred. These data indicate that the remobilisation resulted in an order of magnitude reduction in the phage concentrations at both injection boreholes; probably as a result of mixing and dilution within the borehole water column and as well as increased migration of tracer mass out of the borehole. A final set of samples from the Tracer injection boreholes were collected on the 18th April 2008 close to the end of the sampling regime.

These data indicate that a proportion of the $MS2$ phage tracer was still present at concentrations in excess of background approximately 45 days after injection, and accounts for approximately 20% of that that was left following the 31st March remobilisation. At Comet Way, the $\Phi X174$ phage appeared had returned to concentrations within the range of the natural background (see section 5.4).

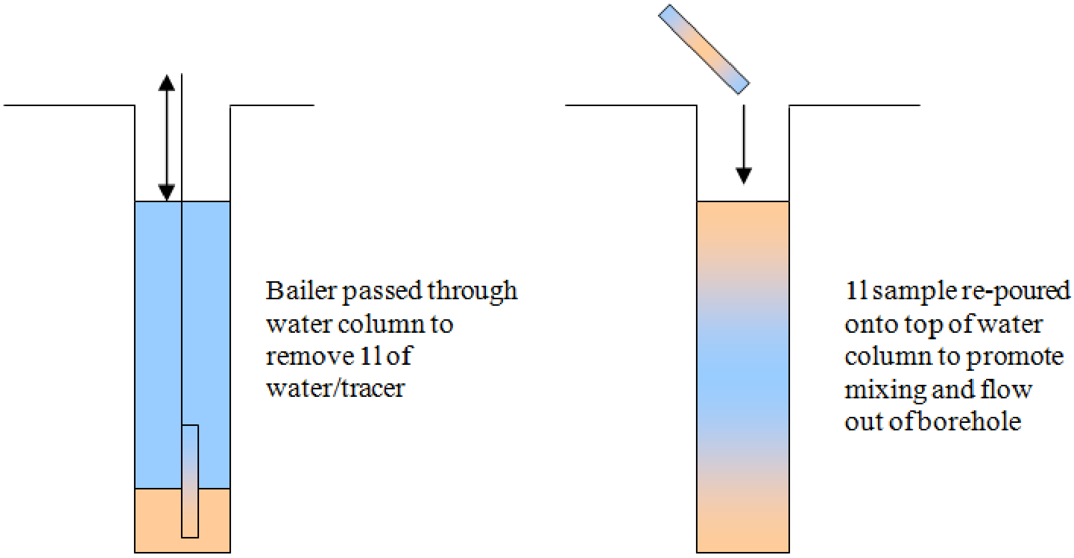


Figure 5.14: Schematic illustration of the injection borehole "re-mobilisation" procedure

5.6.2 Flux of tracer entering aquifer

The tracer injections were intended to provide relatively rapid dosing of the groundwater system and were supported by findings from the single borehole dilution tests at both locations which indicated a return to background levels of electrical conductivity within 8 hours at both Harefield House and Comet Way (Fitzpatrick, 2007) and as was achieved by Skilton and Wheeler (1989) using the same injection method. The loss of tracer from the injection boreholes is plotted against time in figure 5.13 and appears to follow a log-linear decrease with time caused by dilution and migration out of the borehole upon which the exponential inactivation of the phage is probably superimposed.

Estimates of specific discharge derived from the SBDT of the Harefield House and Comet Way observation boreholes has been provided by (Fitzpatrick, 2008) and gives values of 0.17 - 1.3 m/day at Harefield House and 4.4 - 14.7 m/day at Comet Way. Taking the mean specific discharge at both locations gives rates of approximately 0.76m/day at Harefield House and 10.56m/day at Comet Way OBH. Assuming steady state conditions (i.e. a constant flow rate) the theoretical phage concentration in the borehole at time t can be calculated assuming that phage are lost by flux only based on Equations 5.2 and 5.3 for borehole dilution (Halevy et al., 1967) in (Bernstein et al., 2007).

$$q_f = -\frac{V}{\alpha A t} \ln\left[\frac{c}{c_0}\right] \tag{5.2}$$

which can be solved for c by:

$$c = c_0 e^{-\left(\frac{q_f \alpha A t}{V}\right)} \tag{5.3}$$

Where c_0 is the initial concentration, q_f is the specific flux out of the borehole, usually taken to be equal to the specific discharge assuming other flows (e.g. vertical flows or settling) are negligible, α is a shape factor relating to the borehole construction and is typically taken as 2 where there is no gravel pack, A is the surface area of the of borehole and V is the volume. When the estimated concentrations are determined the estimated dilution of all tracer occurs within a few hours at both locations, this is not surprising given the estimated water flux through saturated section of the injection boreholes is between 0.8-5m^3/day and therefore sufficient to replace the water within the volumes of water within the borehole several times over. However this rapid release from the injection sites disagrees with the observed data which suggests phage remained at moderate concentrations within the injection boreholes for several hundred hours after injection. This discrepancy suggests there may be an error in the calculations.

An obvious simplification is that the assumption of even mixing across the saturated length of the borehole is inappropriate, the tracers were intended to be placed at a specific depth to intercept known flow horizons determined from the SBDT of Fitzpatrick (2008). Both Harefield House and Comet Way OBH also have slotted casing which would have restricted the area of flow through which tracer could escape the borehole, however the estimated loss of tracer loss shows greatest sensitivity to the specific discharge. In order to achieve concentrations of similar magnitude to what was observed, a specific discharge on the order of 1×10^4m/day is required and would imply almost stagnant water and very limited migration of tracer.

To determine if, as the dilution test implied, a rapid loss of tracer occurred from the borehole, or as the modelled data imply, relatively little migration a mass balance has been carried out for each injection. The loss from the borehole can be approximated by:

$$M_b(t) = M_0 - M_a(t) - M_i \tag{5.4}$$

Where M_b = Mass in Borehole at time t, M_i = Injection mass, $M_a(t)$ = Total Mass lost to Aquifer at time t, M_i = Mass lost by inactivation at time t which is equal to $M_0 - M_0 10^{-kt}$ where k is the inactivation rate in log_{10} per day. Since the injection mass is known, and the proportion of tracer loss due to decay and inactivation can be estimated based upon the inactivation rates presented in section 5.2.1.1, it is possible to calculate the Mass of tracer lost to the aquifer and thereby define an approximate tracer source term. Sorption is not specifically represented in this approach since it is included in with the mass lost to the aquifer. Rearranging the Mass Balance formula to determine the quantity of tracer in the aquifer at time t gives:

$$M_a(t) = M_0 10^{-kt} - M_b(t) \tag{5.5}$$

An uncertainty in this approach is the degree of mixing within the borehole which influences the measured concentrations used to derive the mass of tracer within the borehole. The sampling of the injection boreholes indicates that injection mixing may have been partial. On this basis, the mass of tracer in the borehole has been determined for each sampling date based on both a fully mixed and unmixed case tables 5.11 and 5.12.

The Inactivation rate k has been taken to be $0.033 \log_{10}$ per day for $MS2$ at 10^oC using the temperature dependent equation for $MS2$ provided by Gerba et al. (1991) and $0.14 \log_{10}$ per day for $\Phi X174$ based on empirical data also provided in Gerba et al. (1991) in the absence of site specific data.

Whilst this approach determines the mass in the aquifer at any one time, this is not a true source term since it describes the total mass of tracer that is in the aquifer not the mass flux of tracer leaving the borehole. Comparing the estimates of total mass remaining in the borehole to that which are estimated to remain active suggests a large proportion of the injection mass must have left the borehole regardless of method used to estimate borehole concentrations and is therefore consistent with the dilution test results. However, this does not explain the relatively high concentrations recorded.

One possibility is that a proportion of the injection mass remained trapped within the injection boreholes, perhaps by sinking to the base of the boreholes, which might easily have occurred given the higher relative density of the glycerol suspension in which the phage were shipped and a similar effect was observed by Skilton and Wheeler (1989). Sinking to the base might then have locally re-concentrated the phage in an otherwise stagnant zone leading to apparently higher concentration.

Table 5.10: Sampling results from injection boreholes. *Assumes injection suspension titration diluted in 21l of groundwater. A specific count could not be achieved for initial Harefield house samples even at 1000 fold dilution indicating that concentrations were in excess of 1×10^6 pfu/ml. ** Two samples were collected on 15/03/2008 to assess the influence of the in-borehole *Waterra* sampling tube, i.e. one from the tube and one with the tube removed.

Location	Phage Species	Time	Date	Concentration (pfu/ml)
Harefield House	MS2	12:24	03/03/2008	$1.43 \times 10^{12*}$
		14:45	15/03/2008	1000000**
		14:50	15/03/2008	1000000**
		11:37	31/03/2008	6.30×10^7
		12:15	31/03/2008	5.20×10^7
		12:31	31/03/2008	7.5×10^6
		15:30	18/04/2008	1.53×10^6
Comet Way	$\Phi X174$	10:55	03/03/2008	$1.9 \times 10^{10*}$
		14:20	15/03/2008	1.3×10^6
		09:12	31/03/2008	7400
		10:50	31/03/2008	1500
		11:37	31/03/2008	240
		15:00	18/04/2008	2

Table 5.11: Loss of $MS2$ phage from the Harefield House borehole

Time (hours)	Active phage M_d (pfu)	Phage in borehole M_b (pfu) Fully Mixed	Unmixed	Phage in Aquifer M_a (pfu) Fully Mixed	Unmixed
0	3×10^{16}	3×10^{16}	3×10^{16}	0	0
671.22	3.59×10^{15}	1.38×10^{12}	6.93×10^{11}	3.58×10^{15}	3.58×10^{15}
671.85	3.58×10^{15}	1.14×10^{12}	5.72×10^{11}	3.57×10^{15}	3.58×10^{15}
672.12	3.58×10^{15}	1.64×10^{11}	8.25×10^{10}	3.57×10^{15}	3.57×10^{15}
1107.10	9.01×10^{14}	3.36×10^{10}	1.68×10^{10}	9.01×10^{14}	9.01×10^{14}

Table 5.12: Loss of $\Phi X174$ phage from the Harefield House borehole

Time (hours)	Active phage M_d (pfu)	Phage in borehole M_b (pfu) Fully Mixed	Unmixed	Phage in Aquifer M_a (pfu) Fully Mixed	Unmixed
291.42	7.982×10^{12}	8.247×10^{10}	1.430×10^{10}	7.900×10^{12}	7.968×10^{12}
670.28	4.921×10^{10}	4.695×10^8	8.140×10^7	4.874×10^{10}	4.913×10^{10}
671.92	4.814×10^{10}	9.516×10^{11}	8.25×10^{10}	4.805×10^{10}	4.813×10^{10}
672.70	4.764×10^{10}	1.523×10^7	2.200×10^6	4.763×10^{10}	4.764×10^{10}
1108.08	1.375×10^8	1.269×10^6	2.200×10^4	1.374×10^8	1.375×10^8

5.7 Results for *Serratia Marcescens* phage

Serratia Marcescens phage was sampled for at 11 locations, the distribution of these locations is indicated in Figure 5.1. Table 5.13 summarises which locations were sampled for *Serratia Marcescens* phage, as well the total number of samples collected, the total number of samples analysed and the number of positive results as well as timing information about each detection.

Table 5.13: Summary of sampling details for the *Serratia Marcescens* phage

Location	No. of Samples			Detection Time (hours)			
	Total	Analysed	Positives	First	Peak	Last	Duration
Hatfield PWS	39	16	4	43.4	43.4	140.8	97.4
Essendon PWS	35	16	10	69.1	69.1	354.6	285.5
North Mymms PWS	13	13	1	214.3	214.3	214.3	-
Arkley Hole Spring	106	38	21	60.6	68.6	357.8	297.2
Lynchmill Spring	125	41	26	93.9	109.9	694	600.1
Chadwell Spring	18	12	0	-	-	-	-
Amwell Marsh PWS	22	8	2	166.4	166.4	212.0	45.6
New River/Amwell Marsh	10	9	3	115.3	115.3	188.9	73.6
Rye Common PWS	6	6	3	166.3	211.8	332.9	166.6
Turnford PWS	21	8	5	166.02	166.02	522.9	356.9
Park Street OBH	9	5	0	-	-	-	-

5.7.1 Hatfield PWS

Of the 39 samples collected from Hatfield PWS, 16 were analysed for *Serratia Marcescens* phage, of these, four tested positive. The results from this analysis are presented in Appendix C and on Figure 5.15(a). Breakthrough at Hatfield PWS occurred between the sample taken at 21.1 hours and the first measured detection of phage at 43.4 hours after injection. This measurement indicated a phage concentration of 230pfu/ml, and was also the peak phage concentration recorded at this location. Phage concentrations had returned to background levels within 96.3 hours of tracer injection. The form of the Breakthrough is a relatively un-dispersed peak with an asymmetric tail. A single further phage detection of 1pfu/ml was sampled at 140.8 hours, however this is at the background level and hence may represent a background detection but the timing and overall breakthrough pattern suggest that it may represent a late arrival of the tracer. The total duration of measured observations was 97.4 hours from first detection until the tracer had returned to background levels.

5.7.2 Essendon PWS

Of the 35 samples collected from Essendon PWS, 16 were analysed for *Serratia Marcescens* phage, of these, ten tested positive. The results from this analysis are presented in Appendix C and displayed in Figure 5.15(b). Breakthrough of tracer at Essendon PWS occurred between the sample taken at 42.5 hours after injection and the first detection of phage 69.1 hours after injection. This measurement indicated a phage concentration of 766pfu/ml and was also the peak phage concentration recorded at this location. The first detection was well in excess of the recorded background range for *Serratia Marcescens* and phage concentrations returned to background within 405.6 hours of the tracer injection. The form of the Breakthrough is a dispersed peak with an asymmetric tail with a secondary peak occurring 140.1 hours after injection. The total duration of the tracer observation was 285.5 hours from first detection until the tracer had returned to background levels.

5.7.3 North Mymms PWS

All of the 13 samples collected from North Mymms PWS were analysed for *Serratia Marcescens* phage. The results from this analysis are presented in Appendix C. A single sample tested positive for *Serratia Marcescens* phage at 214.32 hours after injection with a concentration of 1pfu/ml.

5.7.4 Arkley Hole Spring

Of the 106 samples collected from Arkley Hole Spring, 38 were analysed for *Serratia Marcescens* phage. Of these, 21 tested positive. The results of these analyses are presented in Appendix C and displayed in Figure 5.15(d). Breakthrough of *Serratia Marcescens* tracer at Arkley Hole occurred between the sample taken at 52.6 hours and the first detection at 60.6 hours after injection which indicated a phage concentration of 225pfu/ml. The peak phage concentration of 3360pfu/ml was measured 68.6 hours after the injection. phage concentrations returned to background levels within 237.3 hours of tracer injection .The total duration of the tracer observation was 176.7 hours from first detection until the tracer had returned to background levels, although sporadic occurrences at the background concentration of 1pfu/ml were detected for a further 120 hours. If it is assumed that these sporadic occurrences are low level late arrivals this gives a total duration of observation of 297.2 hours. The form of the breakthrough is a dispersed peak with an asymmetric tail. The tail appears to be a gradual recession with two secondary peaks occurring 148.6 hours after injection, and a larger peak at 192.4 hours.

5.7.5 Chadwell Spring

Of the 18 samples collected from Chadwell Spring, 12 were analysed for *Serratia Marcescens* phage. The results from this analysis are presented in Appendix C, none of these samples tested positive for *Serratia Marcescens* phage.

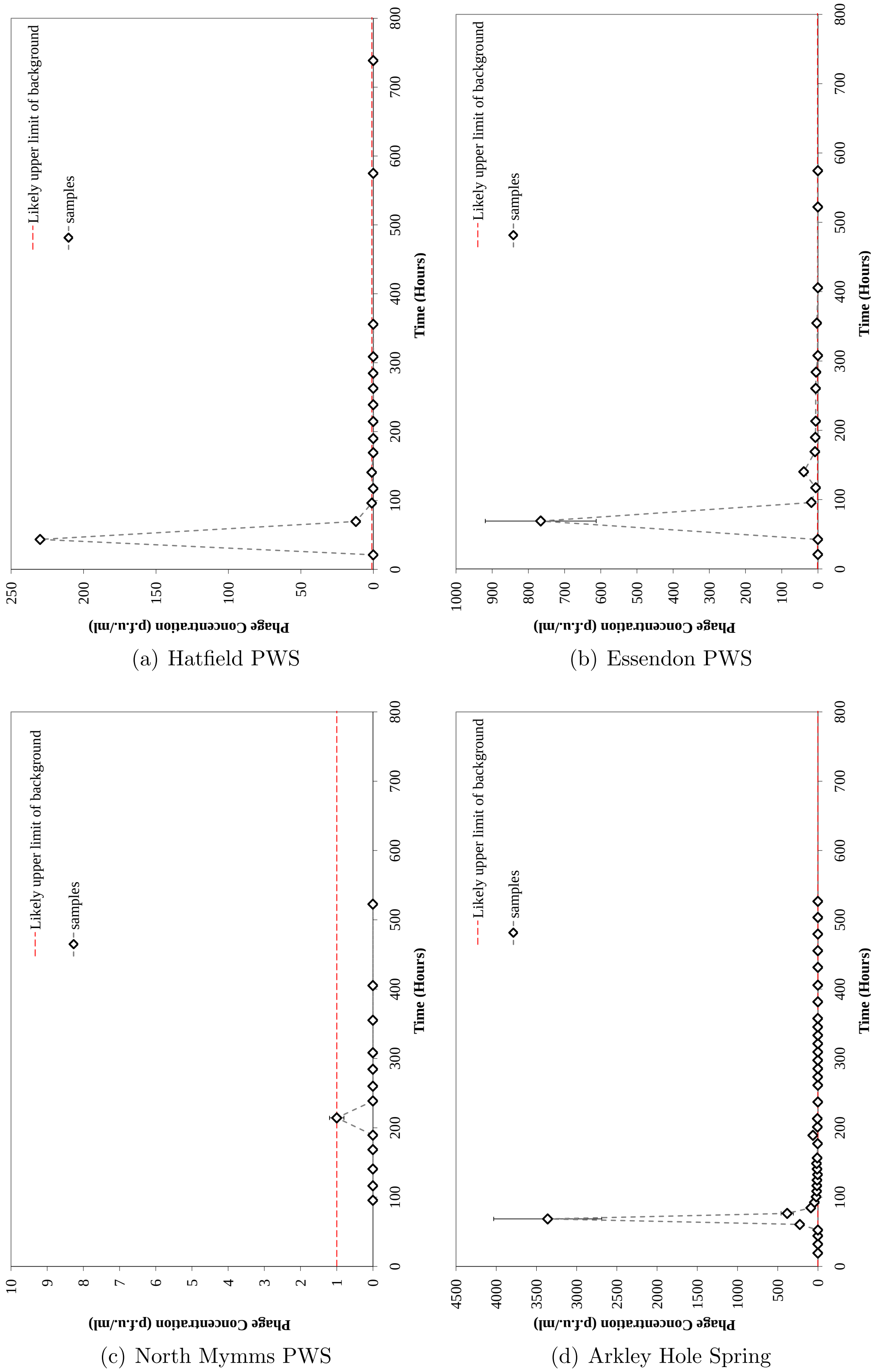


Figure 5.15: *Serratia Marcescens* phage breakthroughs at Hatfield PWS, Essendon PWS, North Mymms PWS and Arkley Hole Spring

5.7.6 Lynchmill Spring

Of the 125 samples collected from Lynchmill Spring, 41 were analysed for *Serratia Marcescens* phage, of these 26 tested positive. The results from this analysis are presented in Appendix C and displayed in Figure 5.16(a).Breakthrough at Lynchmill Spring occurred between the sample taken at 85.9 hours and the first measured detection at 93.9 hours after injection which indicated a phage concentration of 53pfu/ml. The peak measured phage concentration of 1224pfu/ml was sampled 109.9 hours after the injection. The form of the Breakthrough is a dispersed peak with an asymmetric tail. The tail appears to be a gradual recession with a secondary peak occurring 185.06 hours after injection. The total duration from first detection until the tracer had returned to background was 310.86 hours. Sporadic occurrences of *Serratia Marcescens* phage were detected at background concentrations of 1pfu/ml for a further 289.2 hours. If it is assumed that these sporadic occurrences are late arrivals this gives a total duration of observation of 600.1 hours.

5.7.7 Amwell Marsh PWS

Of the 16 samples collected from Amwell Marsh PWS, 8 were analysed for *Serratia Marcescens* phage, of these 2 tested positive. The results from this analysis are presented in Appendix C and displayed in Figure 5.16(b). Breakthrough at Amwell Marsh PWS occurred between the sample taken at 96.4 hours and the first measured detection at 166.4 hours following injection. This sample indicated a phage concentration of 23 pfu/ml, this was also the peak phage concentration recorded at this location. A lower sampling frequency at this location makes it impossible to better quantify breakthrough time. The total duration of the tracer observation was 356.92 hours from first detection until the tracer had returned to Background levels.

In addition to samples collected from the raw water sampling tap of the abstraction well, 9 additional samples were collected from the New River immediately downgradient of the point where the well water is discharged into the New River. this additional sampling was to supplement that of TWUL in order to increase the sampling frequency at Amwell Marsh. Similar phage concentrations were detected, although the data appear to indicate that phage concentrations preceed (or are diluted from) those at Amwell Marsh and it is possible that this might reflect phage concentrations arising in the New River as a result of an upstream source rather than the well discharge, perhaps from Chadwell Spring or the River Lee (for example via Arkley Hole). These data are also illustrated on Figure 5.16(b) and in Appendix C

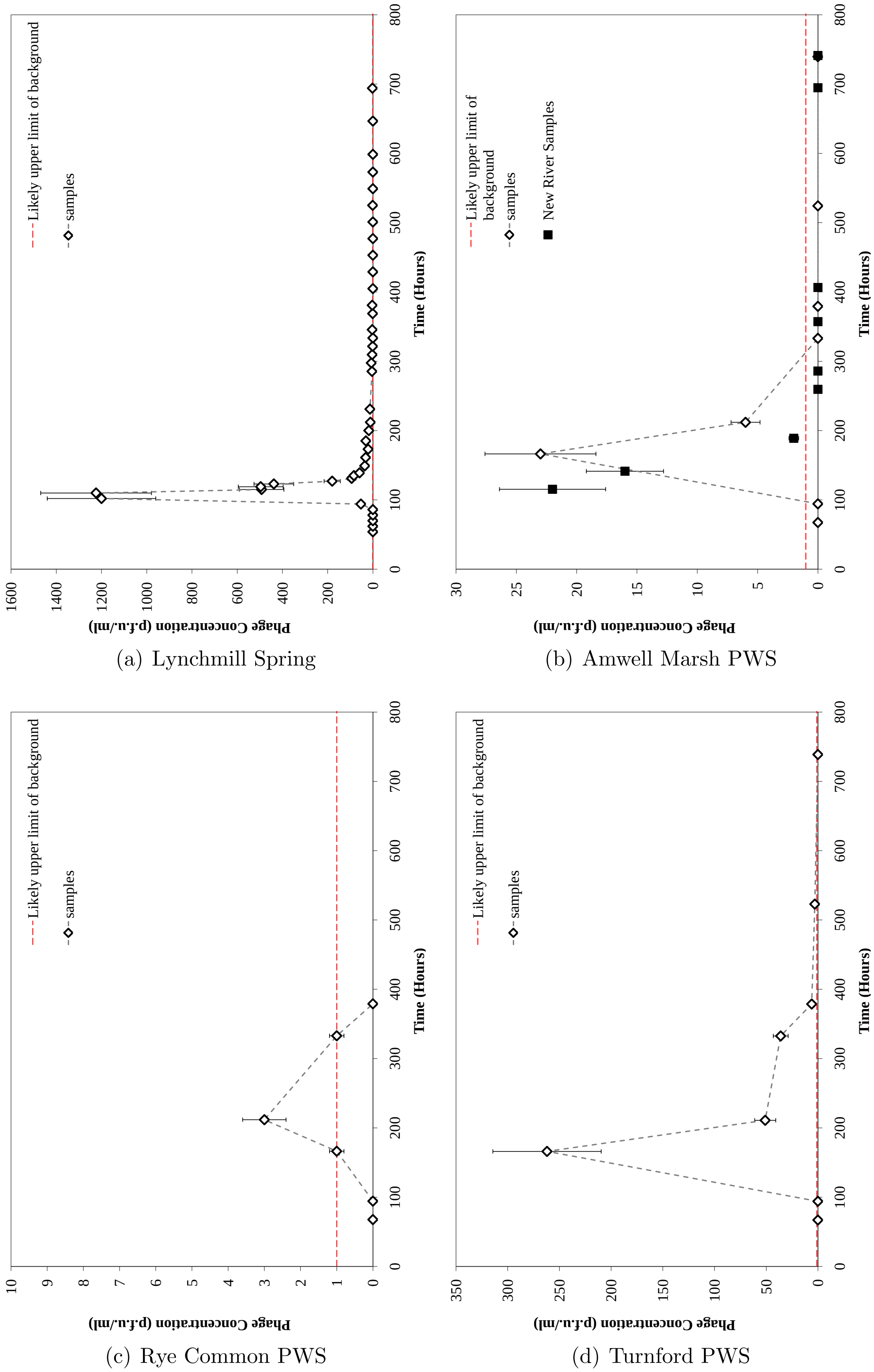
5.7.8 Rye Common PWS

All 6 samples collected from Rye Common PWS were analysed for *Serratia Marcescens* Bacteriophage. Of these, 3 tested positive for *Serratia Marcescens.*

All positives were phage concentrations close to or at the spatial range of the background samples and the limit of detection. The results from this analysis are presented in Appendix C and displayed in Figure 5.16(c). Breakthrough of *Serratia Marcescens* phage, at the spatially observed background concentration of 1pfu/ml occurred at 166.26 hours after injection of the phage. The peak phage concentration of 3pfu/ml was recorded 211.78 hours after the injection. Tracer levels had returned to background levels 332.85 hours after tracer injection. Despite these low concentrations, which are only marginally above the background range, it is considered a breakthrough of *Serratia Marcescens* phage did occur at Rye Common PWS. The pattern of observation, indicating a rising limb, peak and recession (successive sampled phage concentrations of 1, 3, 1) is consistent with observation of a tracer pulse and the timing of the arrival is consistent with other locations nearby (Amwell Marsh and Lynchmill Spring). Owing to the low frequency of sampling at this location (typically every 50-70 hours) there are large intervals at the time of tracer breakthrough and it is therefore possible that higher phage concentrations may have preceded or been detectable in between sampling visits.

5.7.9 Turnford PWS

Of the 21 samples collected from Turnford PWS, 8 were analysed for *Serratia Marcescens* phage, of these, 5 tested positive. The results from this analysis are presented in Appendix C and displayed in Figure 5.16(d). First detection occurred 166.02 hours after injection of the phage at Water End and indicated a phage concentration of 262pfu/ml, this was also the peak phage concentration recorded at this location. Tracer levels had returned to background levels within 522.93 hours following tracer injection. The total duration of the tracer observation was 356.92 hours from first detection until the tracer had returned to background levels.



(a) Lynchmill Spring

(b) Amwell Marsh PWS

(c) Rye Common PWS

(d) Turnford PWS

Figure 5.16: Measured *Serratia Marcescens* breakthroughs at Lynchmill Spring, Amwell Marsh PWS, Rye Common PWS and Turnford PWS

5.8 Results for $\Phi X174$

Eleven locations were monitored for the $\Phi X174$ phage injected at Comet Way, Hatfield. The distribution of these locations relative to the injection point are shown on Figure 5.1. Table 5.14 indicates the total number of samples collected, the total number of samples analysed, and the number of positive results for each location.

Table 5.14: Sampling details for the $\Phi X174$ bacteriophage

Location	No. of Samples		
	Total	Analysed	Positives
Hatfield PWS	39	39	3
Essendon PWS	35	34	8
Arkley Hole Spring	106	66	11
Lynchmill Spring	125	55	22
Chadwell Spring	18	18	1
New River at Kings Mead	7	7	4
New River at Emma's Well	7	7	3
Amwell Marsh PWS	22	22	5
New River at Amwell Marsh	10	9	8
Rye Common PWS	6	3	0
Turnford PWS	21	16	4
Park Street OBH	9	9	0

5.8.1 Hatfield PWS

Given the close proximity of Hatfield PWS to the Comet Way Injection borehole ($\approx$ 1.2km) a possible rapid breakthrough was anticipated and all 39 samples from Hatfield PWS were analysed for $\Phi X174$ phage. The results from these analyses are presented in Appendix C and are displayed in Figure 5.17(a). Of these data, only 3 samples tested positive for $\Phi X174$ phage:

- A sample of 1pfu/ml recovered 217.9 hours after injection
- A sample of 1pfu/ml recovered 355.8 hours after injection
- A sample concentration of 2pfu/ml recovered 790.9 hours after injection

All three positive samples were preceded and succeeded by a number of samples with 0pfu/ml and all are within the likely range of background concentrations of $\Phi X174$.

5.8.2 Park Street OBH

All 9 samples from Park Street OBH were analysed for $\Phi X174$. The results from these analyses are presented in Appendix C. Of these data, no samples tested positive.

5.8.3 Essendon PWS

Of the 35 samples collected from Essendon PWS, 35 were analysed for $\Phi X174$. The results from these analyses are presented in Appendix C and displayed in Figure 5.17(b). Of these data, 8 samples tested positive for $\Phi X174$ phage, the first positive detection was recorded 169.1 hours after injection. The occurrence of $\Phi X174$ at Essendon PWS appears to comprise a series of discrete occurrences at levels equal to, or just above that of the natural background. Only one of these analyses indicated phage outside the likely range of natural background. This was recovered 192.9 hours after injection and gave a $\Phi X174$ phage concentration of 6pfu/ml. This sample was preceded by a concentration of 1pfu/ml at 172.3 hours. Other sporadic occurrences occurred as follows:

- A single sample of 2pfu/ml at 525.4 hours after injection
- Consecutive occurrences of 2 and 1pfu/ml between 669.9 and 695.8 hours after injection
- Further single occurrences of 1pfu/ml at 744.8 hours, 910.9 hours and 1055.8 hours after injection

5.8.4 Arkley Hole Spring

Of the 106 samples from Arkley Hole, 66 were analysed for $\Phi X174$. The results from these analyses are presented in Appendix C and displayed in Figure 5.17(c) and of these data, 11 samples tested positive. When compared with figure 5.17(b), the pattern of occurrence of $\Phi X174$ at Arkley Hole appears to be broadly similar to that of Essendon PWS, comprising a series of discrete occurrences at levels equal to, or just above that of the natural background although none of these results exceeded the likely background range. There also appears to be an overall pattern with slightly higher magnitude and more frequent occurrences in the first 400 hours after injection then less frequent, more sporadic lower magnitude detections thereafter.

- The first detection of $\Phi X174$ occurred 87.8 hours after injection and 2 concentrations of 1pfu/ml were recovered at 87.8 hours and 94.4 hours
- A consecutive set of three detections of 3pfu/ml, 1pfu/ml and 1pfu/ml was recorded at 215.2 hours, 239.2 hours and 263.3 hours
- A consecutive set of 2pfu/ml and 1pfu/ml were recorded at 335.3 hours and 359.7 hours
- Several other discrete but more sporadic concentrations of 1pfu/ml were also recorded

- There appears to be no clear change in $\Phi X174$ concentrations following the phage remobilisation at Comet Way.

5.8.5 Chadwell Spring

All 18 samples collected from Chadwell Spring were analysed for $\Phi X174$ Bacteriophage. The results from these analyses are presented in Appendix C. Only 1 of these samples tested positive for $\Phi X174$ Bacteriophage, giving a concentration of 1pfu/ml at 916.6 hours after injection and ≈ 246 hours after the "remobilisation" of tracer at Comet Way.

5.8.6 The New River

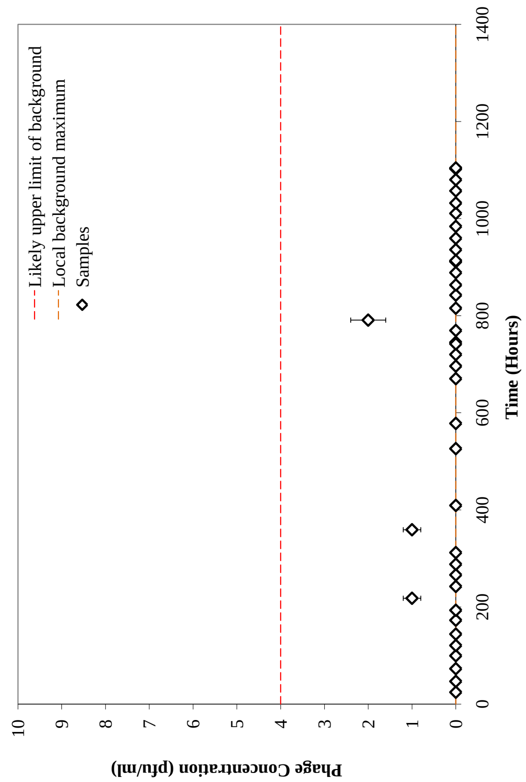
In order to provide additional data, two monitoring sites were added at the New River after the $\Phi X174$ phage remaining in Comet Way Borehole had been remobilised in addition to those samples already collected from the New River downstream of Amwell Marsh PWS. These were 1) at Kings Mead approximately 20m downstream of the Marble Gauge, and 2) close to Emma's Well approximately 200m upstream of the Amwell Marsh PWS discharge point,

- All 10 of the samples taken immediately down stream of the Amwell Marsh PWS discharge point were analysed for $\Phi X174$, of these 9 tested positive.
- 7 Samples were collected from the New River at Kings Mead, all of which were analysed for $\Phi X174$ phage, of these 4 tested positive.
- 7 Samples were collected from the New River at Emma's Well, all of which were analysed for $\Phi X174$ phage, of these 3 tested positive.

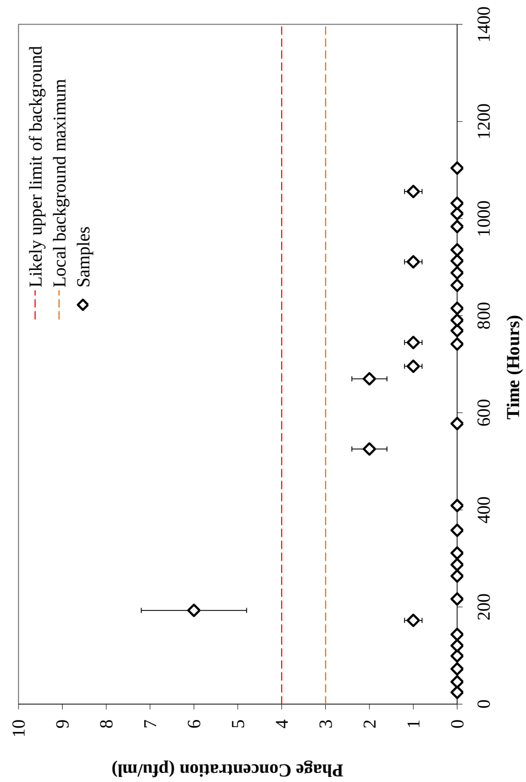
The results from these analyses are presented in Appendix C and displayed in Figure 5.18(a) along with those data from Chadwell Spring.

During the first 700 hours of monitoring only Chadwell Spring and the New River at Amwell Marsh were monitored. For the New River at Amwell Marsh, all but one sample tested positive for $\Phi X174$ phage. The samples ranged between 1 and 4pfu/ml and are higher concentration compared with samples of the Amwell Marsh abstraction well water which could suggest that the source of much of this phage is within the surface waters and the New River itself and not from the borehole discharge which might have implications for the New River samples at Amwell Marsh for Serratia Marcescens since they cannot be directly linked to that of the borehole.

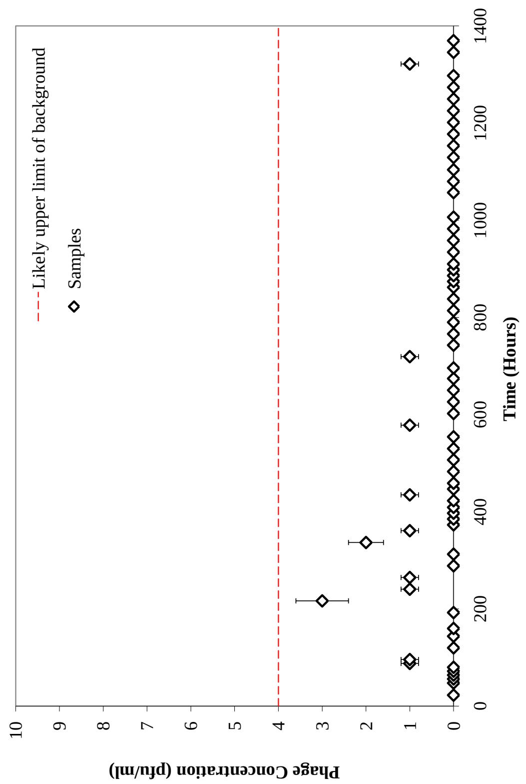
This agrees with data in the later period of monitoring between 700 and 1400 hours which show similar concentrations of $\Phi X174$ in the New River at Emma's Well and Kings Mead, again with variations generally within the regional background range although no clear correlation between Phi X714 concentrations at Kings Mead



(a) Hatfield PWS



(b) Essendon PWS



(c) Arkley Hole Spring

Figure 5.17: $\Phi X174$ phage data at Hatfield PWS, Essendon PWS, and Arkley Hole Spring. The likely upper limit of the background is taken as two standard deviations above the mean background concentration i.e. $\mu + 2\sigma$. Where measured, maximum background concentrations detected at each location are also shown.

or Emma's well appears despite one location being downstream along the New River from the other.

A late sample (1225 hours) for $\Phi X174$ from the New River at Kings Meads does provide a phage concentration in excess of the regionally determined background but is not correlated with high concentrations at any other New River location, or at any of the groundwater monitoring locations.

5.8.7 Amwell Marsh PWS

All 22 samples from Amwell Marsh PWS were analysed for $\Phi X174$. The results from these analyses are presented in Appendix C and displayed in figure 5.18(b). Of these data, 5 samples tested positive for $\Phi X174$ phage. The five samples that tested positive for $\Phi X174$ phage occur in two discrete consecutive peaks, although the sampling interval is relatively in-frequent (approximately every 3 days) and the apparent peaks may not reflect the actual short term variation of tracer.

- The first peak a consecutive concentration of 1, 2, 1pfu/ml occurred between 336.3 and 527.5 hours following injection.
- A higher peak comprising two readings of 3pfu/ml at 866.8 and 888.2 hours following injection.

5.8.8 Lynchmill Spring

Of the 125 samples taken from Lynchmill Spring, 55 were analysed for $\Phi X174$. Of these, 22 samples tested positive for $\Phi X174$ phage. The results from these analyses are presented in Appendix C and displayed in Figure 5.18(c). The first positive detection, a concentration of 2pfu/ml was recorded 164.3 hours after injection. In a similar manner to Essendon and Arkley Hole, the occurrence of $\Phi X174$ at Lynchmill Spring appears to comprise a series of discrete occurrences at levels equal to that of the natural background. None of the samples exceed background concentrations measured both locally and regionally. Based upon the magnitude of detections alone, it is not possible to discern a clear breakthrough from the data since they cannot be clearly distinguished from the background range of phage occurrences. However, some general patterns of occurrence can be observed:

- A consecutive series of occurrences in the order of 1, 3, 4, 1pfu/ml, between 215 and 312 hours following injection.
- A consecutive occurrence of 2, then 3pfu/ml between 432.2 and 456.2 hours following injection
- A consecutive series of occurrences at 1, 2, 1pfu/ml between 601.77 and 625.77 hours following injection

- A consecutive concentration of 1, then 2pfu/ml between 673.76 and 697.25 hours following injection
- A consecutive series of occurrences at of 4, 4, 1pfu/ml between 863.12 and 888.4 hours following injection
- A consecutive occurrence of 1, then 1pfu/ml between 984 and 1008 hours following injection
- A Number of sporadic isolated concentrations of between 1 and 2pfu/ml occur throughout the duration of the monitoring.
- Sporadic single occurrences of 2pfu/ml at 164.3 hours, 2pfu/ml at 528.2 hours, 1pfu/ml at 791.1 hours, 1pfu/ml at 912.4 hours, 1pfu/ml at 1199.78 hours and 1pfu/ml 1247.767 hours.

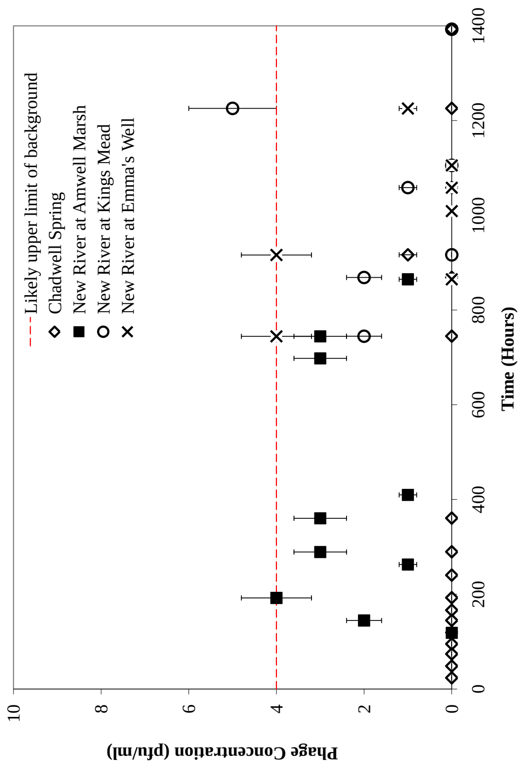
The durations of all multiple concentrations last for approximately 24 hours, possible that some single concentrations lasted longer but for most of these samples testing was limited to 1 sample every 24 hours.

5.8.9 Rye Common PWS

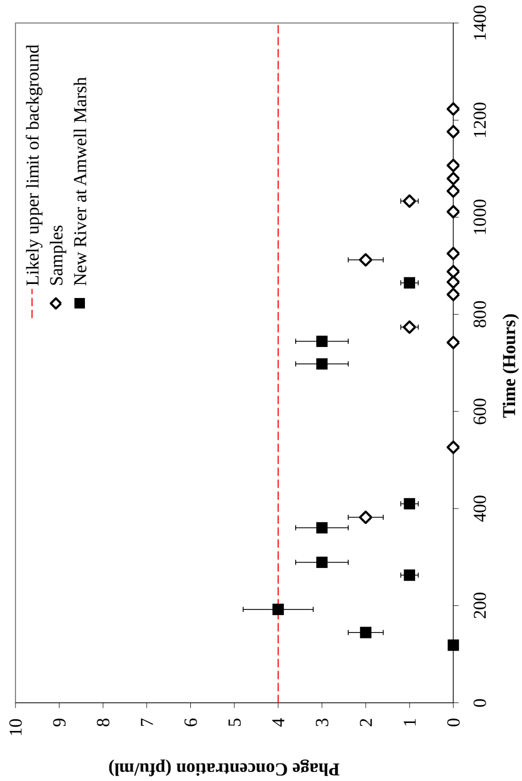
Of the six samples from Rye Common PWS, 3 were analysed for $\Phi X174$. The results from these analyses are presented in Appendix C. Of these data, no samples tested positive for $\Phi X174$ phage.

5.8.10 Turnford PWS

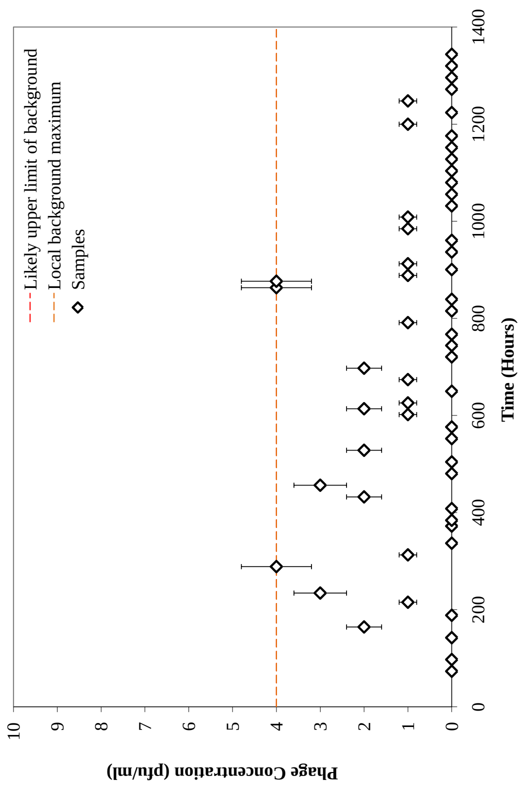
Of the 21 samples taken from Turnford PWS, 16 were analysed for $\Phi X174$ phage. The results from these analyses are presented in Appendix C and displayed in Figure 5.18(d). Of these data, four samples tested positive for $\Phi X174$ phage. The first positive detection was recorded 381.92 hours after injection. As seen at other locations, the occurrence of $\Phi X174$ at Turnford PWS appears to comprise a series of discrete occurrences at levels within the range of the natural background. None of these samples was outside the regional background levels, although no background samples were taken from Turnford PWS to determine local variations to background.



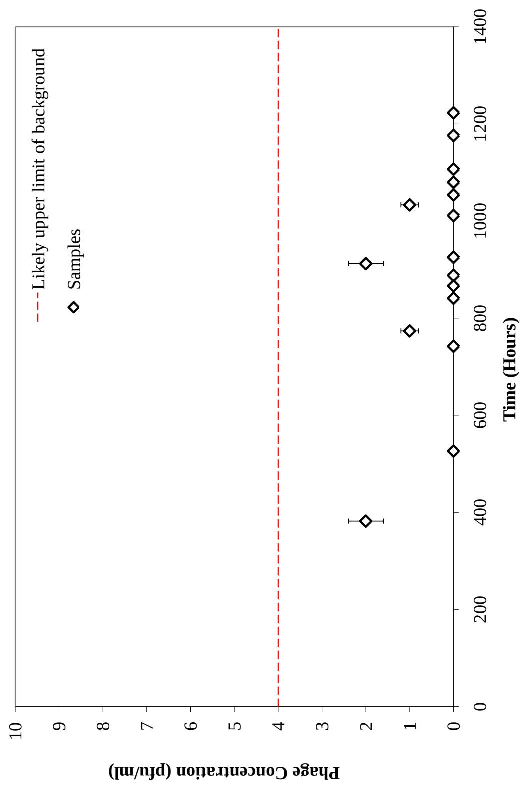
(a) Chadwell Spring and the New River



(b) Amwell Marsh PWS



(c) Lynchmill Spring



(d) Turnford PWS

Figure 5.18: $\Phi X174$ data from Chadwell Spring, The New River, Amwell Marsh, Lynchmill Spring and Turnford PWS. The likely upper limit of the background is taken as two standard deviations above the mean background concentration i.e. $\mu+2\sigma$. Where measured, maximum background concentrations detected at each location are also shown.

5.9 Results for $MS2$

The $MS2$ phage injected at Harefield House, Sandridge was monitored at 19 locations, the distribution of which are indicated in Figure 5.1. Table 5.15 indicates which locations were sampled for $MS2$ phage, the total number of samples collected, the number of samples analysed for $MS2$ and the number of positive results.

Table 5.15: Sampling details for the $MS2$ coliphage Locations

Location	No. of Samples		
	Total	Analysed	Positives
Coleman Green Lane	8	8	1
Nashes Farm	13	13	1
Capps Cottages	13	13	1
Fairfolds Farm	12	12	1
Hatfield Quarry WM8	11	11	1
Hatfield Quarry WM12	11	10	2
Hatfield Quarry WM13	11	10	2
Hatfield Business Park	4	4	0
Hatfield PWS	39	38	2
Essendon PWS	35	33	9
Arkley Hole Spring	106	58	8
Lynchmill Spring	125	53	13
Chadwell Spring	18	16	3
New River at Kings Mead	7	7	1
New River at Emma's Well	7	7	3
Amwell Marsh PWS	6	0	0
New River at Amwell Marsh	10	9	3
Turnford PWS	21	14	1
Park Street OBH	9	4	0

The pattern of results for each location is discussed in more detail in the following sections.

5.9.1 Locations in the Vale of St Albans

Eight locations were monitored in the Vale of St Albans for $MS2$ phage and comprised private abstraction wells and observation boreholes, the distribution of sampling locations is presented in Figure 5.1. The results from these analyses are presented in Appendix C to and are shown on Figure 5.19(a).

Of the 81 samples taken in the Vale of St Albans only 9 samples tested positive for $MS2$ phage, The positive phage concentrations are for the most part sporadic single concentrations of 1pfu/ml. Only two samples gave phage concentrations above 1pfu/ml and only a single sample gave phage a concentration outside the likely range of background concentrations.

- A sample from Hatfield Quarry Observation Borehole 25.03 hours after injection giving a concentration of 2pfu/ml, outside the locally determined range of 1pfu/ml but within the whole regional background range

- A sample from Hatfield Quarry Observation Borehole WM12 746.43 hours after injection giving a concentration of 8pfu/ml, this was followed by a concentration of 1pfu/ml at 865.85.

5.9.2 Hatfield PWS

Hatfield PWS is the closest major groundwater discharge point to the $MS2$ injection point at Harefield House, 38 of the 39 samples collect at Hatfield PWS were analysed for $MS2$ phage, the results from these analyses are presented in Appendix C and displayed in Figure 5.19(b). Of these data, only 2 tested positive; a concentration of 1pfu/ml was detected at 191.8 hours and another concentration of 1pfu/ml at 357.7 hours following injection.

5.9.3 Essendon PWS

Of the 35 samples collected at Essendon PWS 33 were analysed for $MS2$ phage, the results from these analyses are presented in Appendix C and displayed in Figure 5.19(c). Of these data, 9 tested positive for $MS2$ phage. This comprised 7 concentrations of 1pfu/ml and 2 samples with concentrations of 2pfu/ml. These data are within the likely range of the background but the two concentrations of 2pfu/ml exceed the local background detected at Essendon PWS. The concentrations are generally sporadic and relatively common at 1pfu/ml, however a number of sequential detections occur.

- A concentration of 1pfu/ml at 262.2 hours followed by a concentration of 2pfu/ml at 285.7 hours.

- 2 concentrations of 1pfu/ml at 407.5 hours and 524.0 hours, followed by a concentration of 2pfu/ml at 668.6 hours and a further concentration of 1pfu/ml at 694.4 hours, although it is recognised that the sampling interval is irregular and has long gaps between analysis so the sequential nature of these concentrations may be coincidental.

5.9.4 Arkley Hole Spring

58 of the 106 samples from Arkley Hole were analysed for $MS2$ phage. The results from these analyses are presented in Appendix C and displayed in Figure 5.19(d). Of these data, 11 samples tested positive for $MS2$ phage. When compared with the data for Phi X174 the pattern of occurrence of $MS2$ at Arkley appears to be broadly similar, comprising a series of discrete occurrences at levels within the range of the natural background although none of these results exceeded the local or regional background range. Only 2 of the samples gave concentrations above 1pfu/ml forming two discrete peaks.

- A concentration of 1pfu/ml at 312.7 hours followed by a concentration of 3pfu/ml at 335.3 hours returning to 0 p.f.u. at 371.7 hours but a further occurrence of 1pfu/ml occurred at 395.7 hours. This overlaps with a sequential set of Phi X174 phage breakthrough between 335 - 359 hours suggesting that either a common cause, such as rainfall or background might be responsible rather than tracer.

- A peak of 2pfu/ml at 552.8 hours followed by 1pfu/ml at 576.8 hours. This overlaps with a sporadic concentration of 1pfu/ml Phi X174 at 576.8 hours.

5.9.5 Chadwell Spring

16 of the 18 samples collected from Chadwell Spring were analysed for $MS2$ Bacteriophage. The results from these analyses are presented in Appendix C and displayed in Figure 5.20(a). Three of these samples tested positive for $MS2$ Bacteriophage, giving a concentration of 1pfu/ml on all three occasions at 359.4 hours, 743.5 hours and 867.6 hours. Despite occurring sequentially, there are large gaps between sampling intervals and these data are well within the likely range of natural background concentrations.

5.9.6 The New River

As with Phi X174 a number of sites along the New River were sampled for $MS2$ phage:

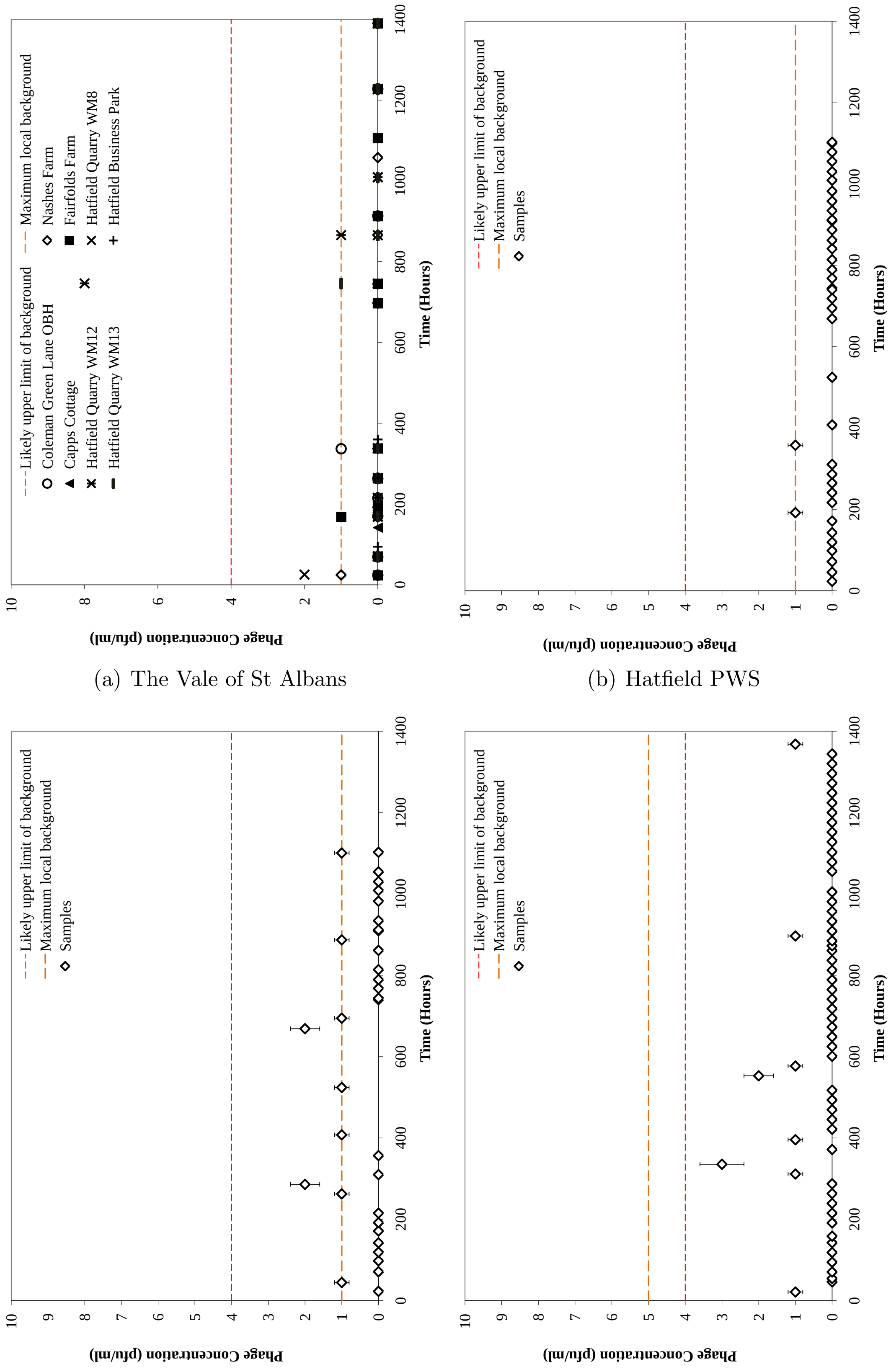
- 9 of the 10 of the samples taken immediately down stream of the Amwell Marsh PWS discharge point were analysed for $MS2$ phage, of these 3 tested positive.

- 7 Samples were collected from the New River at Kings Mead, all of which were analysed for $MS2$ phage, of these 1 tested positive.

- 7 Samples were collected from the New River at Emma's Well, all of which were analysed for $MS2$ phage, of these 3 tested positive.

The results from these analyses are presented in Appendix C and displayed in Figure 5.20(a). In general, the concentrations in the New River for $MS2$ phage appear less frequent and slightly lower for the same locations compared to that for $\Phi X174$ phage. They are also sporadic and less consistently above the detection limit of 1pfu/ml with none of the sites giving a consecutive detections above detection limits.

- At Amwell Marsh a sample tested positive for 8pfu/ml in excess of the background range after 190.8 hours and two further samples both of 2pfu/ml at 359 and 743 hours.



(a) The Vale of St Albans

(b) Hatfield PWS

(c) Essendon PWS

(d) Arkley Hole Spring

Figure 5.19: $MS2$ phage data from the Vale of St Albans, Hatfield PWS, Essendon PWS, and Arkley Hole Spring. The likely upper limit of the background is taken as two standard deviations above the mean background concentration i.e. $\mu + 2\sigma$. Where measured, maximum background concentrations detected at each location are also shown.

- At Kings Mead 1 samples gave concentration of 1pfu/ml at 1224 hours
- At Emma's Well 2 samples gave concentrations of 1pfu/ml at 863 and 1224 hours and a single sample of 2pfu/ml at 1056 hours.

5.9.7 Amwell Marsh PWS

20 of the 22 samples collected from Amwell Marsh PWS were analysed for $MS2$ Bacteriophage. The results from these analyses are presented in Appendix C and displayed in Figure 5.20(b). Of these samples only 2 samples tested positive for $MS2$ phage:

- A sample of 1pfu/ml at 335 hours, two further samples taken following this sample but were not analysed for $MS2$ phage and were disposed of before re-testing could be arranged, this would have correlated with a peak of Phi X174 phage between 336 and 527 phage.
- A single sample of 2pfu/ml at 886.9 hours preceded and followed by a number of samples at 0pfu/ml. None of these samples exceeds the regionally determined background range.

5.9.8 Lynchmill Spring

Of the 125 samples from Lynchmill Spring, 53 were analysed for $MS2$ phage. The results from these analyses are presented in Appendix C and displayed in Figure 5.20(c). Of these data, 13 samples tested positive for $MS2$ phage. In a similar manner to Essendon and Arkley Hole for both Phi X174 and $MS2$ phage, the occurrence of $MS2$ at Lynchmill Spring appears to comprise a series of discrete occurrences at levels equal to that of the natural background. None of the samples exceeds the likely range of background concentrations, especially given that Lynchmill Spring showed the highest background concentrations for $MS2$. Based upon the magnitude of detections alone it is not possible to discern a clear breakthrough from the remaining data since the observed data cannot be clearly distinguished from the background range of phage occurrences. However, some general patterns of occurrence can be observed:

- Discrete peaks of 1pfu/ml at 140.8 hours, 287.23 hours, 550.3 hour, 789.75 hours, 1054 hours, 1150 hours and 1246 hours following injection
- A double consecutive sample of 1pfu/ml at 719.15 and 742.6 hours following injection
- A single sample of 4pfu/ml at 861.75 hours following injection, this was also a sample with 4pfu/ml Phi X174

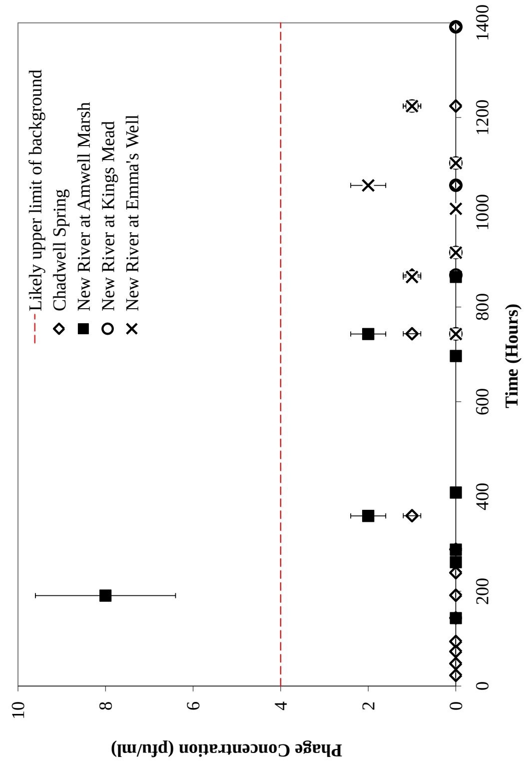
- 4 consecutive samples that vary between 1pfu/ml and 2pfu/ml between 1246 and 1318 hours following injection As for $\Phi X174$ testing for $MS2$ was limited to 1 sample every 24 hours, on some occasions where consecutive concentrations were suspected either due to a positive detection or due to relatively high concentrations elsewhere analysis was increased to every 12 hours.

5.9.9 Turnford PWS

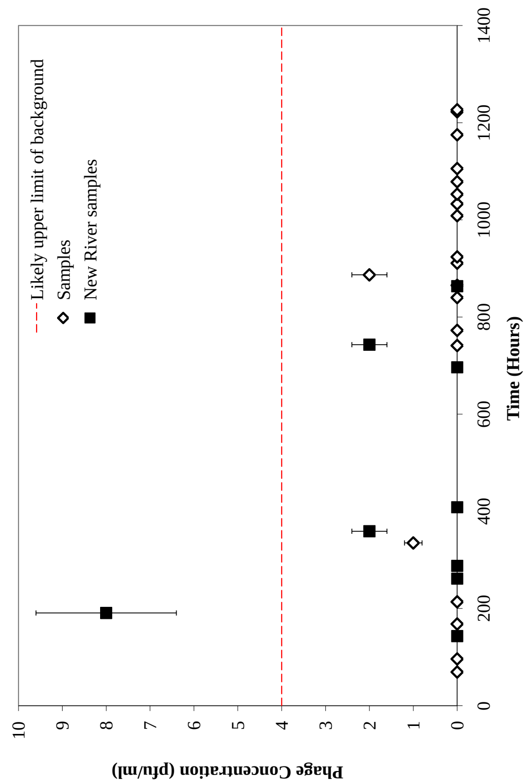
14 of the 21 samples from Turnford were analysed for $MS2$ phage, the results from these analyses are presented in Appendix C. Of these data, only 1 sampled tested positive; a concentration of 1pfu/ml was detected at 772.32 hours following injection.

5.9.10 Park Street

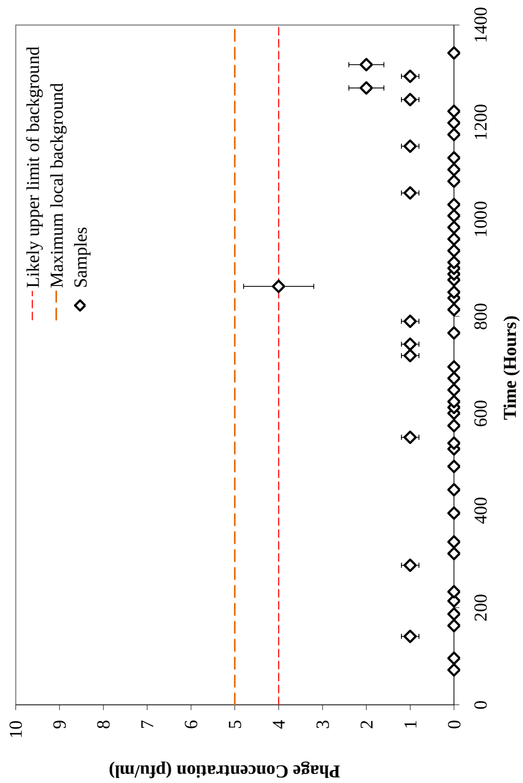
4 of the 9 samples from Park Street OBH were analysed for $MS2$ phage. The results from these analyses are presented in Appendix C. Of these data, no samples tested positive for $MS2$.



(a) Chadwell Spring and the New River



(b) Amwell Marsh PWS



(c) Lynchmill Spring

Figure 5.20: $MS2$ Coliphage data from Chadwell Spring, The New River, Amwell Marsh and Lynchmill Spring. The likely upper limit of the background is taken as two standard deviations above the mean background concentration i.e. $\mu + 2\sigma$. Where measured, maximum background concentrations detected at each location are also shown.

5.10 Discussion of Results

5.10.1 Serratia Marcescens

Based upon the results presented in Section 5.7, Figure 5.21 indicates the locations which have shown positive detections of Serratia Marcescens phage in excess of background concentrations and which are connected to the Water End swallow holes. This comprises 7 of the 11 locations where samples were analysed for the phage.

Connections from the Water End swallow holes were established by (Harold, 1937) and the pattern of connection and observations in this tracer test is consistent with that seen previously. In addition, the present tracer test extends the range of observation of tracer further west to include Hatfield PWS and Essendon PWS and also further south along the Lee Valley to include Turnford PWS

Essendon PWS and Hatfield PWS, which were not sampled at the time of 20th Century tracer tests, appear to have intercepted either karstic conduits directly or have developed a link to fissures which are directly connected to the karstic system, and supports the inferred karstic connection from turbidity data at Essendon PWS. The confirmed connection of Hatfield PWS to the karstic flow system might also be indicative of the mechanism by which scavenge pumping at this location can influence bromate concentrations at down-gradient locations.

The observed pattern of occurrence covers the entire length of Palaeocene feather edge between Water End and the southern Lee Valley. It is possible that the subsurface geometry of the Hertfordshire karst flow system can be considered to crudely follow the exposed surface karst and the Palaeocene Feather Edge and that rapid groundwater flows should be expected within this corridor.

Detectable levels of tracer outside the likely background range were not identified at North Mymms PWS, Park Street OBH and Chadwell Spring and the majority of samples at these locations had no detectable *Serratia Marcescens* phage. At North Mymms PWS this is in agreement with the 20th century monitoring at this discharge point suggesting that the discharge from the Water End swallow holes migrated north and east and not to the abstraction wells in the south.

In comparison with the 20th Century tests, the non detection at Chadwell Spring is a major difference since this was the principal monitoring and breakthrough point for all 4 tests conducted in the 1920's and 1930's. Non-detection at this location might reflect a change in the flows within the aquifer, possibly as a result of abstraction or lowering of water levels which may reduce the component of flow to this location derived from Water End. The non-occurrence of tracer at Chadwell Spring is discussed further in Section 5.10.5.

A negative result from tracer testing does not necessarily imply that there is no connection since the sampling regime was discontinuous. Breakthrough of tracer below the detection limit (of 1pfu/ml) may also have occurred. The first sampling

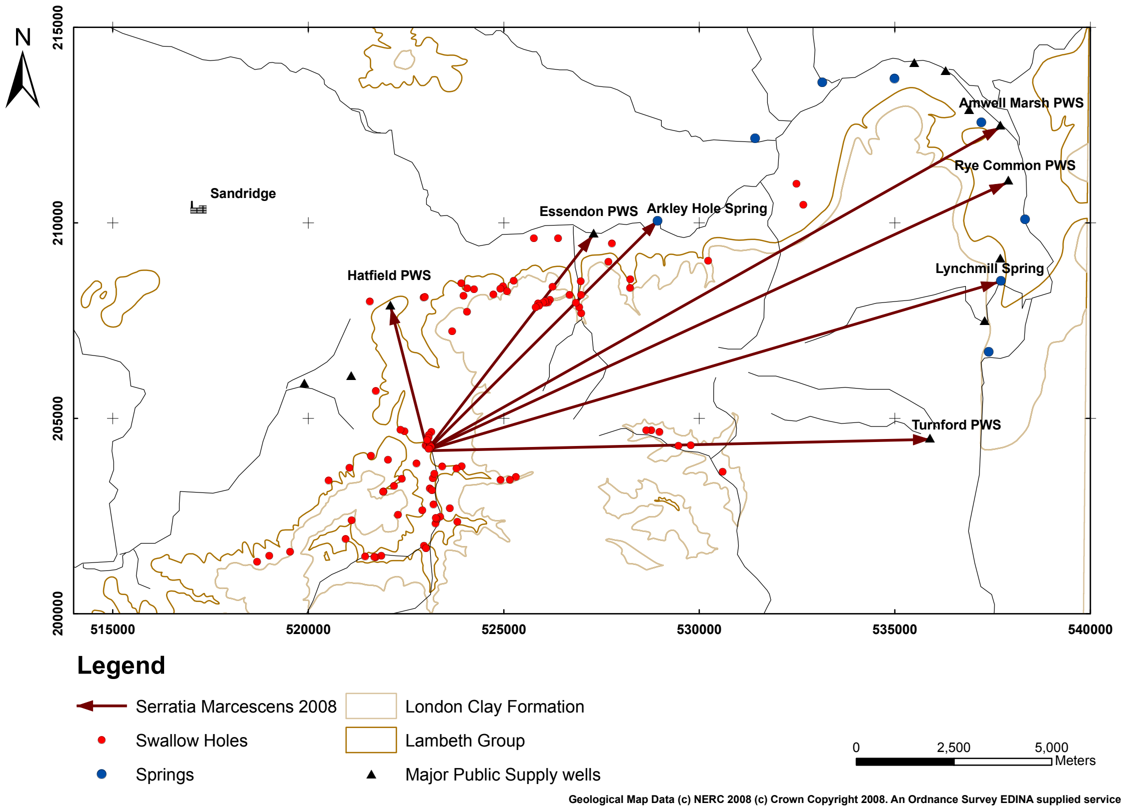


Figure 5.21: Locations which show concentrations of *Serratia Marcescens Phage* above the likely range of background concentrations and hence are likely to be connected to flows entering the Water End Swallow Holes

at North Mymms PWS did not occur until 95.42 hours following injection. Given the close proximity of North Mymms PWS to the Swallow Holes at Water End (approximately 600m) it is also possible that the slug of tracer arrived quickly and had been extracted by the pumping well to below detectable limits prior to the first sample. The timing, in this case, would be consistent with the breakthrough seen at the next closest sampling location, Hatfield PWS, where first detection occurred after 43 hours and had returned to background concentrations within 96 hours. However, due to the tortuous geometry of karstic networks, the straight line distance from the injection point cannot necessarily be used as an indicator of connectivity or the likely travel time.

5.10.1.1 Arrival Times and Groundwater Velocities

As well as the qualitative information offered by establishing the connection of sampling locations to the Water End injection point, more quantitative information about the aquifer can be determined from comparison of tracer travel times. The calculated travel times for each location are presented in Table 5.16, the New River at Amwell Marsh is excluded since it is not certain of the source or travel distance for the tracer measured at this location.

Due to the discrete nature of the sampling regime, and the 1pfu/ml detection limit it is impossible to be certain of the actual breakthrough time of tracer at each

Table 5.16: Measured *Serratia Marcescens* phage tracer travel times and comparison with the Flourescein tracer breakthroughs of (Harold, 1937). When compared both tracer tests show very similar breakthrough times even allowing for differences in tracer and detection method.

Location	Time (Hours after injection)				
	Breakthrough	Peak	Average	Last	Harold (1937)
Hatfield PWS	43.4	43.4	44.9	96.3	-
Arkley Hole	60.6	68.6	72.8	237.3	60
Essendon PWS	69.1	69.1	79.7	405.6	70-91
Lynchmill Spring	93.9	109.9	115.9	321.95	72-96
Amwell Marsh PWS	166.4	166.4	175.8	333.1	91-95
Turnford PWS	166.02	166.02	195.7	738.77	-
Rye Common PWS	166.3	211.8	226.9	332.9	-

monitoring location, however this can in part be constrained to the time between which tracer reached detectable limits which is bounded by the last negative sample and the first detection.

This pattern of arrival suggests a sequential arrival of tracer with increasing distance from the injection point consistent with the movement of tracer along the Palaeocene Feather Edge from the injection point.

At Hatfield PWS, Essendon PWS, Amwell Marsh PWS and Turnford PWS the first measured occurrence was also the peak measured occurrence although in actuality it is likely that the peak occurrence was missed and occurred earlier.

At Essendon PWS, the first detection at 69.1 hours was similar to that of Arkley Hole at 60.6 hours after injection. Essendon PWS is located at a closer distance to Water End ($\approx$ 6.8km to Essendon and $\approx$ 8.1km to Arkley Hole) but is nearby and in similar a geological setting within Chalk outcrop close to the River Lee below the Palaeocene Feather Edge. It is possible that Essendon may be drawing water from the already established natural karstic discharge to Arkley Hole in this area.

Based upon the closer distance, the arrival of tracer at Essendon PWS might have preceded that of Arkley Hole but was missed by the daily sampling interval. However, since the actual route of transport cannot be determined and the karst flow paths may follow tortuous routes, distance cannot necessarily be used as an indicator of relative arrival times.

The largest uncertainty is for the timing of breakthrough of tracer at the NNR wells due to a gap in sampling regime between $\approx$ 94 hours and $\approx$ 166 hours following injection. As a result, the measured arrival times for these locations are similar however it is likely that differing distances and aquifer conditions meant that actual arrival at these locations was not. It is at least certain that breakthrough at Lynchmill Spring preceded that at the NNR wells since first detection at this location was prior to the last negative sample at the NNR wells.

Sampling of the New River at Amwell Marsh suggests that first arrival at this location could be further constrained to between 94 and 115 hours if the New River sample downstream of Amwell Marsh PWS is assumed to be representative of, or influenced by, the borehole discharge.

The overall duration of tracer observation above background levels in general increased with distance from the injection point, which is suggestive of increased dispersion with transport distance.

Essendon PWS is unusual in that it shows a much longer persistence of tracer above background concentrations than every other location except for Turnford PWS despite a moderate discharge rate of nearly 5Ml/day. It is possible that Essendon may be abstracting from either a larger proportion of the karstic conduit network (e.g. through direct connections) or there are a greater proportion of slower flow-paths that discharge to Essendon PWS or that flow paths to Essendon PWS are subject to more dispersion, which may include dual porosity processes.

The longest duration of observation above background levels was at Turnford PWS where tracer persisted for over twice as long as most other locations. This is most probably due to Turnford PWS not being actively abstracted during the tracer test and therefore tracer monitoring was more indicative of the natural groundwater movement at this location and not that affected by pumped discharge.

Tracer arrival times from the early 20th century tracer test are presented in Table 5.16. Although it is interesting to consider the differences, they are not strictly directly comparable since the nature of the tracers is different. Phage are non-conservative particulate tracers, compared to dissolved flourescein, a number of studies have also indicated that bacteriophage show faster apparent breakthrough than conservative tracers in aquifers of interstitial porosity but shows similar behaviour to fluorescent dyes in karstic and surface water tracing (e.g. Rossi et al., 1998).

The largest difference in timing is probably due to the two tracers having different detection limits and observation methods which might serve to give different results in terms of the measured breakthrough and observation times. The early 20th century tracer tests were largely qualitative based upon the presence or absence of fluorescence in the sample under UV light which is likely to be less sensitive the quantitative phage measurement. In addition whilst sampling intervals for the 2008 tracer test are known, such details are not available for the 20th century tests.

The aquifer conditions are also not well known for the early 20th century tests and although the time of year is similar which could allow for seasonal variations (e.g. in recharge/water levels), the range of abstractions, water levels and perhaps the degree of karst development may be different than during the present test.

Despite the differences outlined above, comparison of the data suggests that the timing of arrival of tracer in the 2008 test appears to be similar to that when compared for the same location in the historical tests (Chadwell Spring excluded). The main difference appears to be that travel times to locations in the Lee Valley are slightly slower, although they are within the range of values previously established. A possible mechanism for this may be the lowering of hydraulic gradients along the

Table 5.17: Apparent Straight Line Velocities of *Serratia Marcescens* from Water End

Location	Distance	Velocity (km/day)			
	(km)	Breakthrough	Peak	Average	Last
Hatfield PWS	3.2	1.77	1.77	1.71	0.80
Arkley Hole	8.1	3.21	2.83	2.67	0.82
Essendon PWS	6.8	2.36	2.36	2.05	0.40
Turnford PWS	13	3.32	2.84	2.69	0.97
Lynchmill Spring	15.3	2.21	2.21	2.09	1.10
Amwell Marsh PWS	16.6	2.40	2.40	2.04	0.54
Rye Common PWS	16.4	2.37	1.86	1.73	1.18

transport flow paths caused by abstraction and drawdown from Hatfield PWS and Essendon PWS.

The duration of observations cannot be directly compared since in the only case where the last observations were recorded in the 20th Century tests the tracer was injected in pulses over a period of four days which differs in methodology to the present test. The other injections, which were similar to the present method did not record the timing of last observation of tracer.

5.10.1.2 Transport Velocities

Based upon the transport distance, an apparent straight line velocity for the tracer can be determined, these have been calculated and are presented in Table 5.17. In reality, the true tracer velocities are likely to be faster than this since the transport distances will follow longer following tortuous flow paths, Field and Nash (1997) suggest that actual distance travelled may be up to 1.5 times the straight line distance.

The range of velocities for first arrivals is between 1.77 and 3.32km/day, the fastest being to Turnford PWS, the slowest to Hatfield PWS. Peak transport velocities range from 1.77 to 2.84km/day. These velocities are similar to those recorded for rapid groundwater flow in the Chalk aquifer at other locations in South East England (Atkinson, 1977; Banks et al., 1995; Maurice et al., 2006, e.g.). A tracer velocity-distance plot is presented in Figure 5.22.

The velocities are interesting when considering the actual flow path taken by the tracer, if, as is suggested by the pattern of arrival and supporting evidence (see sectionsec:karst), the subsurface karstic conduits follow the pattern of surface karst developed along and beneath the Palaeocene feather edge the transport distances from Water End would be longer than the straight line distances and therefore the apparent groundwater velocities will be higher than that determined.

5.10.1.3 Form of the Breakthrough

The form of a tracer breakthrough is indicative of the dispersion, dilution, retardation and inactivation of the tracer as it has migrated to discharge points. Examining

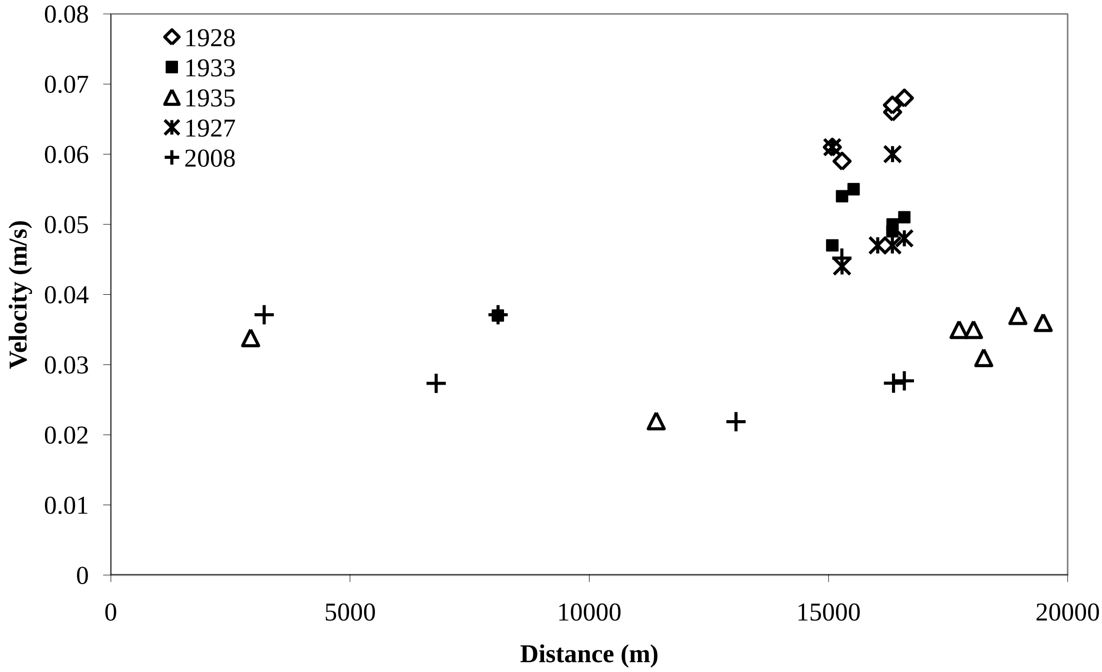


Figure 5.22: Velocity distance plot for the *Serratia Marcescens* breakthroughs and those of Harold (1937).

the graphical plots presented in section 5.10.1, the general form of all breakthroughs for the *Serratia Marcescens* phage is similar. The breakthrough comprises a rapid rise to peak concentration, well above background levels and a slower asymmetric decline to background levels as a result of dispersion, either mechanical or due to Dual-porosity exchange with the chalk matrix, other possible factors could also include temporary sorption or storage such as in stagnant zones or microfractures.

Sampling of the rising limb prior to the measured peak concentration only occurred at Arkley Hole, Lynchmill Spring and Rye Common. It is likely for other locations the sampling frequency was of an insufficient resolution to define the rising limb. The duration between initial detection and the observed peaks at Arkley Hole and Lynchmill Spring ($\leq$ 24 hours) is shorter than the sampling interval at all other locations and since the duration of the declining limb is longer, it is likely that first measurement occurred somewhere on the declining limb of tracer breakthrough.

In part, the rate of decline, and the overall magnitude of breakthrough will be influenced by the discharge rate at each location as this will influence the rate of mass recovery and the dilution of tracer by mixing with tracer free waters, however for the most part this will reflect variations in the dispersion (which are typically related to travel distance), retardation and decay of the tracer on the way to the discharge points.

Table 5.18: Relation of approximate discharge rate, peak concentration and length of tracer recession - defined as the time interval from peak observed concentration until background concentrations are reached

Location	Discharge (Ml/day)	Peak Concentration (pfu/ml)	Length of Recession (hours)
Hatfield PWS	6	230	52.83
Arkley Hole	10	3360	168.7
Essendon PWS	5	766	238.7
Turnford PWS	0	262	572.75
Lynchmill Spring	3.8	1224	211.6
Amwell Marsh PWS	20	23	166.7
Rye Common PWS	15	3	121.1

5.10.1.4 Secondary Peaks

A number of secondary peaks and steps are visible on the declining limb of the Tracer breakthrough curves, these secondary peaks are presented on Figure 5.23.

- At Essendon PWS a secondary peak (A on figure) of 39pfu/ml was sampled at 140.1 hours, this peak was preceded by a sampled concentration of 6pfu/ml and followed by a sampled concentration of 8pfu/ml. The magnitude of the peak islarger than the ±20% estimated precision on the analysis and therefore is probably a genuine feature rather than measurement error.

- There is a secondary peak at Arkley Hole (B on figure) of 16pfu/ml, after 148.6 hours. This was preceded by a sample indicating 9pfu/ml at 140.6 hours, and followed by a sample indicating 8pfu/ml at 156.6 hours.

- A much larger secondary peak (C on figure) of 62pfu/ml occurs at Arkley Hole after 189.2 hours, this was preceded by a sampled concentration of 3pfu/ml at 177.2 hours and followed by a sample of 5pfu/ml at 189.2 hours.

- There is a step and minor peak in the Lynchmill Spring recession over three samples collected between 115 and 123 hours after injection when sampled concentrations consecutively were analysed at 492, 496, 438pfu/ml. However, given that the likely precision on the data is ±20% (effectively ±100pfu/ml) it is uncertain if this feature is genuine or is a result of error on a number of relatively quickly taken samples.

- A secondary speak at Lynchmill Spring (D on Figure) is observed after 185 hours, giving a phage count of 31pfu/ml, preceded by a sample with 21pfu/ml and followed by a sample of 18pfu/ml, again this is outside any 20% error (±6pfu/ml) and so is likely to be a genuine feature.

- Later times between 300 and 400 hours after injection show a number of small fluctuations, between 1-10pfu/ml at all three locations, although some of these variations are within assumed range of error (20%) and hence may be but the

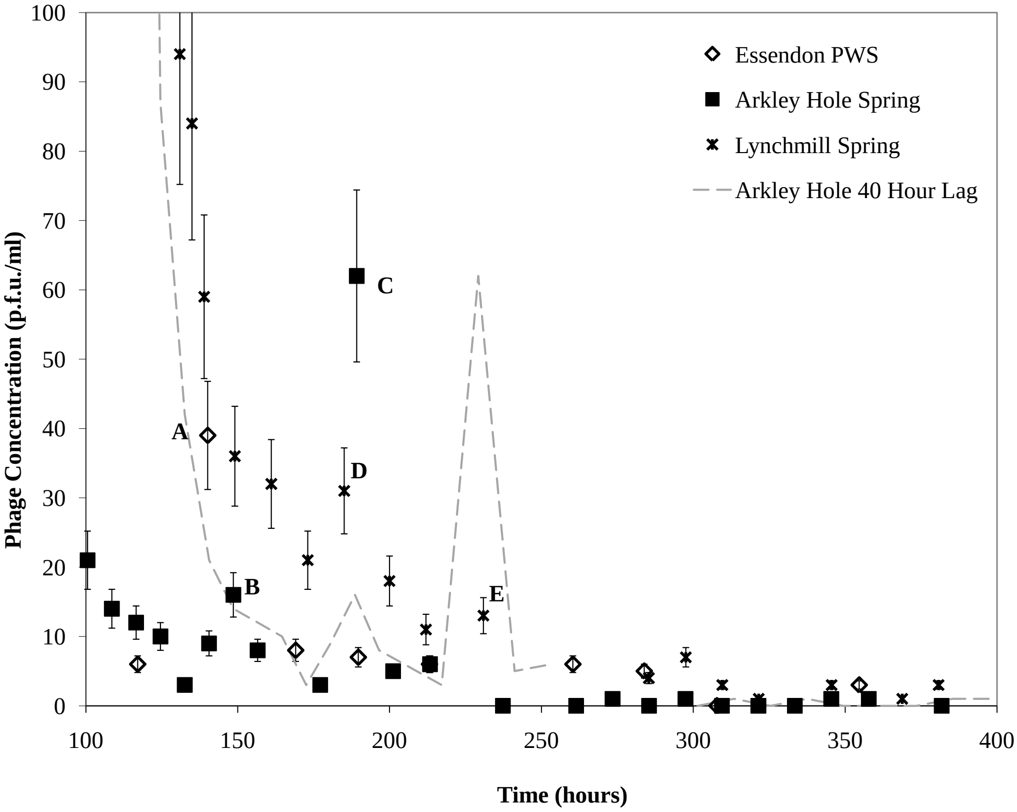


Figure 5.23: Secondary peaks on recession of *Serratia Marcescens* phage at Essendon PWS, Arkley Hole and Lynchmill Spring. Note when the Arkley Hole breakthrough curve is shifted by 40 hours (grey line) the similarity in form to that of Lynchmill Spring suggesting that the secondary peaks might be due to a common cause upstream of both locations.

similarity in the form of fluctuation between locations suggest that they could are a genuine feature perhaps with a common origin.

The exact cause of these peaks is uncertain as there are number of possible mechanisms that could lead to their generation;

- Additional flushing of the residual tracer that had become trapped or temporarily sorbed in the surface water (Water End/Mymmshall Brook System) or unsaturated zone.

- Changes in discharge at the outflow point that might have a diluting or concentration effect upon measured tracer concentrations. This could either be through decreased flow of water from sources other than the karst system that might have little or no resident tracer and therefore the overall dilution would reduce. Or an overall reduction in flow from these non tracer bearing sources which would cause to concentrate tracer from tracer bearing sources.

- Discharge from multiple pathways between Water End and the sampling point, for example the presumed conduit network might have multiple non-interacting pathways that reach peak breakthrough at differing times

A combination of these effects might also produce the observed breakthrough.

The timing of the secondary peaks to some extent mirrors the order of the initial breakthrough, with first occurring at Essendon and then Arkley Hole and Lynchmill Spring. It is possible that the first secondary peak to occur (feature A at Essendon at $\approx$ 140 hours and feature B at Arkley Hole at $\approx$ 148 hours) may be the same feature an the peak has travelled further along the karst flow system and possibly even to Lynchmill Spring (feature D). Features C at Arkley Hole and E at Lynchmill Spring may also be similarly related by the same 40 hour shift (Figure 5.23).

The pattern of secondary peak occurrence is similar to that of the breakthrough from initial injection and suggests a lagged shift in time with distance from source it is probable that the secondary peak is a characteristic form of the breakthrough that originates upstream of Essendon, Arkley Hole and Lynchmill Spring. The most likely origin being a secondary input of tracer close to the injection site that has travelled along the same flow-paths as the initial tracer pulse.

Rainfall and recharge might be important in both controlling the flushing of tracer and causing changes in discharge rate, particularly at springs where this is uncontrolled. After a relatively dry preceding period over 20mm of rain was recorded between 8th and 10th of March 2008 (see section 5.4.1.1), coving the period of approximately 106 - 178 hours following injection. It is possible that this rainfall if it entered the karst groundwater system as recharge, either at Water End or through more local swallow holes developed along the Palaeocene boundary that it could have influenced measured phage concentrations and could be the cause of the major secondary peaks at all three locations.

The difference in magnitude might be explained by the difference in distance and travel time between these locations and the source which would cause increased dispersion to Lynchmill Spring. This pattern would then be consistent with the variation in concentration being caused by a near source mechanism (e.g. recharge/flushing of the swallow holes) rather than a local influence at the discharge point.

These features are unlikely to be confined just to the discharge locations at which they were monitored. It is possible that secondary peaks in concentration may have occurred at other locations but were not detected as the sampling regime was not frequent enough, or alternatively higher discharge at some locations may have diluted and smoothed out such peaks so that they cannot be distinguished from the overall pattern.

5.10.2 Recovery

To allow a more direct comparison of the tracer breakthroughs, it is possible to estimate the total recovery of tracer based upon the known abstraction rates obtained from TVW and TWUL and the sampled concentrations of tracer. Since discrete samples were at approximately regular time intervals rather than continuous measurement of a variable, in order to make mass balance calculations several assumptions must be made to account for the degree of accuracy of tracer detection imposed by the error and uncertainty.

- The first measured detection is assumed to be equal to the actual breakthrough, in reality first measurement is likely to be slower than the actual first, and often the peak arrival. This assumption will therefore under-estimate the actual amount of tracer recovered at the monitoring point. However, since peak tracer concentrations and actual breakthrough times are unknown an improved estimate is not possible.

- It must also be assumed that the peak measured concentration is equal to the actual peak concentration, again since there is no way of knowing what the actual peak concentration was this will also under-estimate recovery since it is unlikely that sampling time coincided with peak arrival.

- Measured/sampled concentrations reflect the bulk concentrations of groundwater, i.e. the sampled water is evenly mixed, this is probably appropriate for most abstraction locations since mixing will occur in the borehole water column, it may be less appropriate for springs since mixing may be uneven in discharge pools and could vary depending upon the relative flows in the feeding fissures.

- Discharge is assumed to be constant over each given averaging time period (i.e. between sampling times). Where data are available to indicate that discharge varies from day to day (such as at Hatfield PWS and Essendon PWS) the hourly discharge rate has been averaged to calculate the total abstraction during that sampling interval.

- The tracer is assumed to be conservative and not subject to inactivation following sampling prior to analysis. Although measures were taken to ensure sample preservation, some inactivation of the samples will occur following collection and therefore the measured concentrations will underestimate the true concentration at time of sampling, again this will result in an under-estimate of the recovery. If the inactivation rates were known this could be corrected for.

- Discharges from spring Locations (i.e. Arkley Hole ($\approx$ 120l/s) and Lynchmill Spring - $\approx$ 30l/s) are estimated based upon visual observations, or where available for Arkley Hole on spot flow gauging in 2006 (Atkins, 2006) and were not recorded directly during the tracing. Changes in spring discharge due to rainfall etc were not recorded and so an average rate is assumed for the duration of sampling.

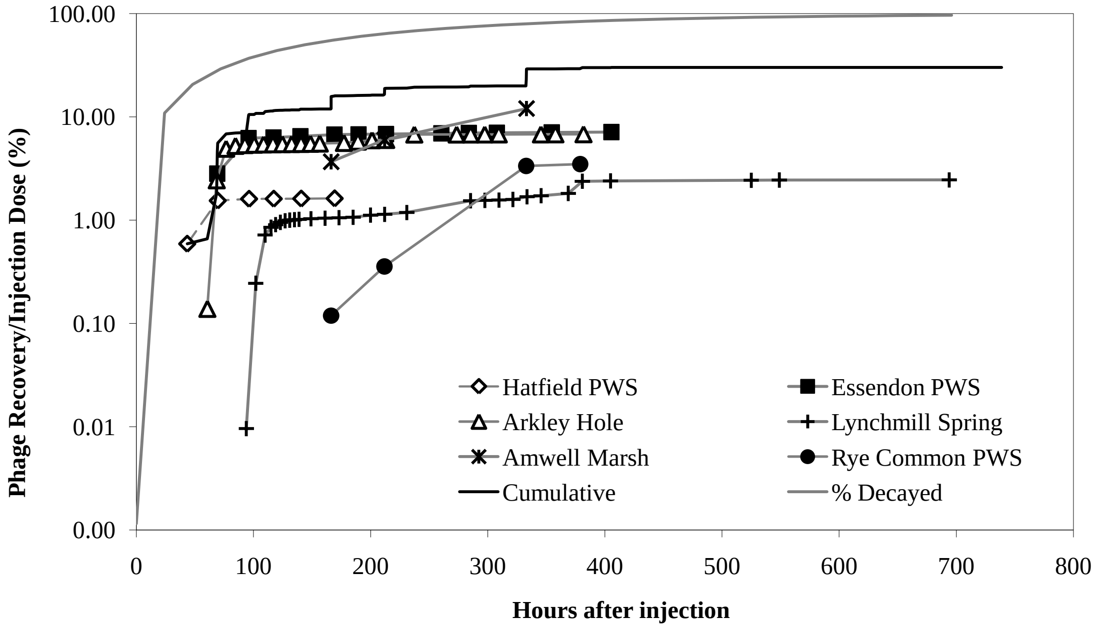


Figure 5.24: Recovery of *Serratia Marcescens* phage at monitoring locations

Recovery from the New River at Amwell Marsh has been excluded since occurrences cannot be easily distinguished between that occurring from the discharge into the New River from Amwell Marsh PWS and upstream inputs such as the diversion of the River Lee, and by way of the river, discharge from Arkley Hole and any that might have occurred from Chadwell Spring, this eliminates double counting of the phage.

Decimals resulting from the calculation method are rounded to the nearest integer since phage are discrete objects and it would be impossible to recover 0.5pfu of phage.

The method for estimating recovery is based upon the total recovery and is corrected for the abstraction at each discharge point by multiplying the recovery in one ml by the total abstraction. The proportion of recovery is compared to the total number of phage injected, i.e 3×10^{15}pfu/ml. The mid points of the integral trapezoids have also been used to estimate mean transport times for tracer to each location.

Bacteriophage are also prone to inactivation which will naturally reduce the amount of available phage within the aquifer with time. Assuming an inactivation rate for *Serratia Marcescens* phage of $0.05 \log_{10}$/day derived from Wimpenny et al. (1972) this would suggest that during the 600 hours where *Serratia Marcescens* phage were detected around 95% of the injection mass would have become inactive by the end of sampling period. Incorporating this inactivation, the recovery of the proportion of available tracer has also been estimated and is presented in Table 5.19 for both conservative and non conservative cases. A plot of the recovery with time is presented in Figure 5.24, Turnford PWS has been omitted from this plot for clarity.

Table 5.19: Estimated recovery of *Serratia Marcescens* phage tracer for a conservative case and incorporating phage inactivation based upon a rate derived from Wimpenny et al. (1972)

Location	Discharge (Ml/day)	Recovery		
		Total (pfu)	Conservative	With Inactivation
Essendon PWS	2 - 5	1.36×10^{14}	4.53%	7.1%
Arkley Hole	10	1.29×10^{14}	4.29%	6.8%
Amwell Marsh PWS	20	1.11×10^{14}	3.76%	12.04%
Hatfield PWS	6	3.63×10^{13}	1.21%	1.62%
Lynchmill Spring	2.6	2.31×10^{13}	0.77%	2.45%
Rye Common PWS	15	2.3×10^{13}	0.77%	3.49%
Turnford PWS	0	2.37×10^{6}	0.00%	3×10^{-7}
Total Recovery		4.59×10^{14}	15.3%	33.5%

When corrected for abstraction the total recovery in the conservative case is estimated to be approximately 15% of the total injection of phage tracer and when inactivation is incorporated this increases to over 33%. Essendon and Arkley hole have the two largest recoveries of phage this may indicate a stronger connection to the karst system as well as a shorter travel distance and therefore less dispersion and decay of the phage.

The influence of discharge at abstraction wells is apparent, with relatively high recovery at Amwell Marsh PWS which has by far the largest discharge of any location although the overall magnitude of measured phage concentrations was lower than any other location except for Rye Common PWS. Rye Common has the fifth smallest recovery and also had the lowest overall measured concentration due to dilution of concentrations at the high abstraction rate (15Ml/day).

In effect, the recovery at Turnford PWS is almost zero because the well was not actively abstracting water during the tracer test. Recovery has has been estimated from the number of sample bottles collected with positive results (i.e. 16×100ml).

When recovery is corrected for abstraction and decay, the sampling locations appear to account for approximately 33% of the available tracer. Essendon and Arkley Hole again have a relatively high overall recovery and show a similar mass recovery profile possibly indicating that the transport routes to these locations are similar as is also bourne out by bromate concentrations.

Abstraction rate and arrival time also appear to be an important control with Amwell Marsh and Rye Common having the highest abstractions and despite the relatively late arrival of tracer at these locations ($\approx$ 55% had decayed by the time of first detection) these locations were still able to recover a relatively large proportion of the tracer pulse by their large abstractions.

If Turnford is excluded, Hatfield PWS, where breakthrough occurred earliest, recovered the lowest proportion of the available tracer by the end of the first 100 hours following injection. By the end of the period which at tracer was detectable at Hatfield PWS, approximately 40% of total tracer mass had decayed and thus the majority of the injection mass was still available during this time. This could indicate the connection with Hatfield PWS is less well developed than other locations since with the tracer plume less dispersed shortly after injection, a strong connection would probably have recovered a large proportion of tracer mass.

Approximately 85% of the tracer injection mass is unaccounted for, this tracer has either sorbed, become in-active or has discharged to locations not monitored by the sampling regime. It is likely that a large proportion has been sorbed or diluted below detection limits within the aquifer. Some may also have discharged via baseflow, to the River Lee and might have occurred via groundwater baseflow along the length of Lee between Hatfield and the Lee Valley. Other possible sinks for tracer are to private borehole abstractions or due to sporadic abstractions from NNR wells which were not monitored such as Amwell Hill. It is also possible that a proportion of the tracer may have bypassed the River Lee to the east or entered the unconfined aquifer to the south.

5.10.3 $\Phi X174$ Phage

Delineating and characterising the breakthrough of $\Phi X174$ from the Comet Way Borehole at sampling locations carries considerably more uncertainty compared to the occurrence of the *Serratia Marcescens* Phage. Measured occurrences of $\Phi X174$ are generally discrete single occurrences or rather than continuous coherent tracer breakthrough curves and are at or close to the likely range of background concentrations. Of all the data, only two samples showed $\Phi X174$ phage concentrations in excess the measured range of background concentrations.

- A sample taken 192.9 hours after injection at Essendon PWS giving a phage concentration of 6pfu/ml
- A sample taken 1225.7 hours after injection collected from the New River, Kings Meads giving a phage concentration of 5pfu/ml

Despite being outside the measured range the background concentrations, when analytical accuracy ($\pm$20%) giving errors of approximately 1pfu/ml and 1.2pfu/ml) is taken into account, neither of these samples is outside the regional background range although the Essendon PWS sample still exceeds the background range detected locally (0pfu/ml).

The rising and falling pattern of phage concentration for the sample that exceeded background concentrations (0, 1, 6, 0pfu/ml) at Essendon PWS as well as the exceeding the likely range of background concentrations suggest that this detection could potentially represent be a low level short duration breakthrough of tracer from the Comet Way Borehole. Over the transport distance from Comet Way (5.6km) this would suggest a straight line transport velocity of $\approx$ 786m/day to first arrival and 700m/day to the peak arrival (6pfu/ml), this is generally consistent with karstic transport speeds in the Chalk but is somewhat slower than travel times

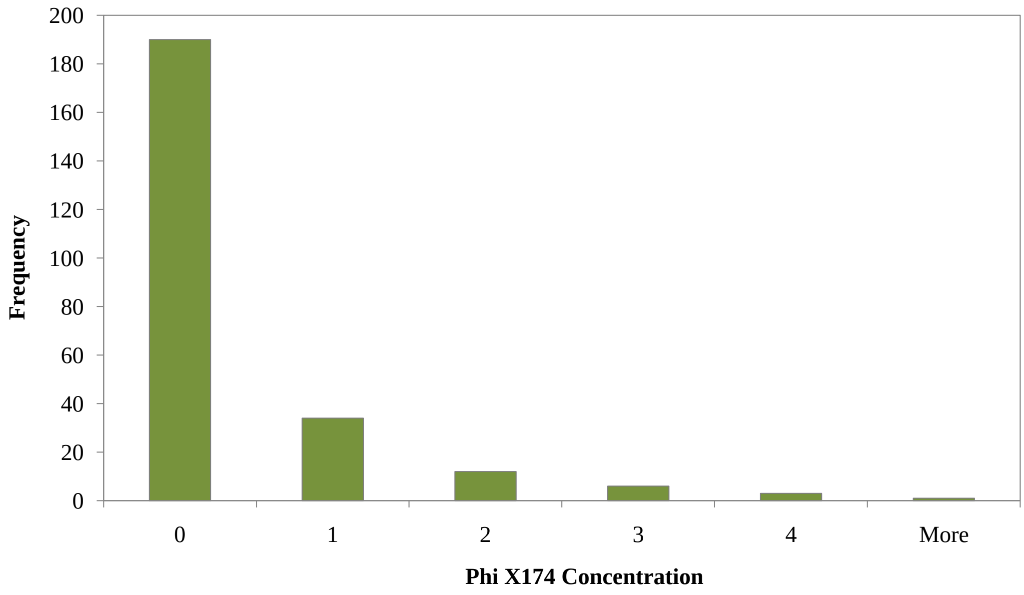


Figure 5.25: Histogram of $\Phi X174$ tracer test samples (background samples are excluded)

Table 5.20: Comparison of the descriptive statistics of the background $\Phi X174$ samples and those taken after tracer injection suggest they cannot be distinguished based on concentrations alone.

Sampling Regieme		Background	Tracer Test
No of Analyses		15	246
Concentration	Minimum	0	0
(pfu/ml)	Mode	0	0
	Mean	0.73	0.43
	Maximum	4	6
	Standard Deviation	1.39	0.75
Likely Upper Limit	95% of samples	4	2
	99% of samples	5	3

over similar distances indicated by the *Serratia Marcescens* phage injected at Water End.

Statistical data for all $\Phi X174$ samples are presented in Table 5.20 and a histogram of the sampled concentration distribution is presented in Figure 5.25.

The summary statistical data suggest that there is not a clear distinction between the tracer test data and the background data since a single exception above 5pfu/ml would be expected in every 370 samples, in the case of the tracer test this occurs once in 246 samples and therefore it cannot be clearly established that this apparent breakthrough represents a departure from background. The overall range of tracer concentrations appears narrower than that of the background, in part this could be due to the relatively small background sample size compared to that of the tracer test and the determined background distribution may be incorrect. Examination of a normal probability plot (Figure 5.26) for the tracer test data suggest that they do not conform to a normal distribution at the 5% significance level and that the data exhibit skewness to the right and higher values might be expected to occur more frequently.

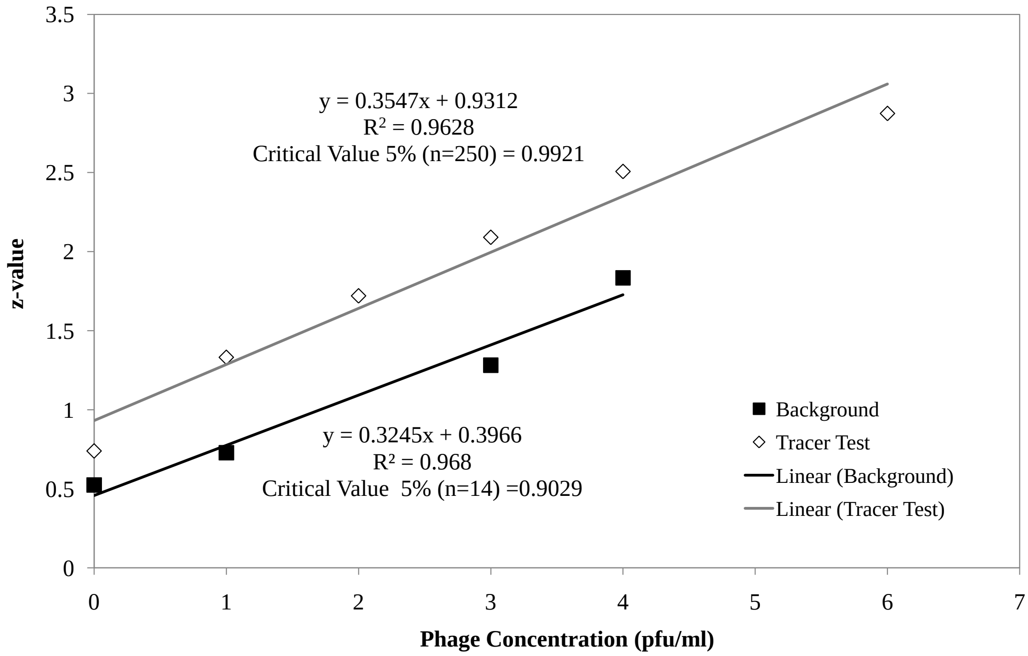


Figure 5.26: Normal Probability plot of the $\Phi X174$ tracer test and those of the natural background. The tracer test data do not conform to a normal distribution at the 5% significance level and exhibit positive skewness to the right (skewness statistic= 3.93)

Since a breakthrough cannot be clearly distinguished in terms of magnitude alone consideration must therefore be given to the pattern of phage occurrence to identify if any are consistent spatially (e.g. with a migrating pulse or plume of tracer) and temporally e.g. patterns of arrival at similar times forming discrete peaks. Low concentrations of bacteriophage tracer breakthrough of similar magnitude (2pfu/ml) to those observed in this tracer test have been successfully delineated in the Chalk aquifer of Hertfordshire from relatively arbitrary injection points (Price et al., 1992). In that case although no background data were collected, multiple tracers were used and breakthrough of phage tracer occurred at a similar time to a dye tracer.

5.10.3.1 Duplicate Sampling of $\Phi X174$

Additional sampling at Essendon PWS and Hatfield PWS by Three valleys Water on several occasions; 03/04/2008, 10/04/2008 and 18/04/2008 meant that some samples were collected within a few hours of each other. These samples might be indicative of the short term variability as well as variation in detection limits.

The data showed minor variations, with variable results between 0 and 1 for samples collected at similar times. These variations are within the range of analytical error ($\pm$20%) as well as the likely range of natural background and itmight indicate that background concentration is variable over shorter timescales than the normal sampling interval.

5.10.3.2 Non Detections of $\Phi X174$

Easier to consider than breakthroughs, are locations at which either phage concentration of $\Phi X174$ were persistently below detection limits or were sporadic and generally below, rather than at background levels.

- At Hatfield PWS, only 3 of 39 samples had measurable concentrations of $\Phi X174$ phage ranging from 1 to 2pfu/ml. All positive detections were non-continuous.
- At Park Street OBH, none of the 9 samples had measurable concentrations of $\Phi X174$ phage.
- At Rye Common PWS, none of the 3 samples analysed had measurable concentrations of $\Phi X174$ phage.
- At Turnford PWS, only 4 of the 16 samples had samples had measurable concentrations of $\Phi X174$ phage ranging from 1 to 2pfu/ml. All positive detections were discrete and non-continuous.

As with the *Serratia Marcescens* phage, a negative result (non detection of tracer) does not necessarily imply that there is no connection, since the sampling regime was discontinuous at each location therefore phage breakthroughs may have been missed. In addition, dilution or breakthrough of tracer below the detection limit (1pfu/ml) may have occurred.

However for these locations, given the magnitude of phage occurrence, and the temporal variation and style of occurrence (i.e. in isolated discontinuous samples) it is considered that $\Phi X174$ tracer did not reach any of these locations.

5.10.3.2.1 Hatfield PWS At Hatfield PWS, only three samples out of 39 had measurable levels of $\Phi X174$ phage, these were discrete, non continuous detections of 1 or 2pfu/ml, the other 36 samples gave concentrations of 0pfu/ml. Locally at Hatfield PWS, 2 background samples both of 0pfu/ml. Thus the detections at Hatfield PWS are above the locally determined background concentration but are below the regionally determined background range.

It is possible that given the close proximity of Hatfield PWS to Comet Way OBH that rapid flow from the injection borehole to the abstraction borehole could have occurred in the first 24 hours after injection prior to the first initial sampling of Hatfield PWS. However, there is limited evidence to support this since none of the early samples from Hatfield PWS gave any concentrations of $\Phi X174$ which might suggest a tail of tracer (although dispersion over this distance and time might be minimal in a karst flow path).

The concentration of 2pfu/ml at 790.9 hours after injection is higher than any previous detection at Hatfield PWS (The two earlier occurrences and no detection during background sampling). The count of 2pfu/ml occurred approximately 130 hours after the remobilisation of Tracer at Comet Way.

A possibility is that this higher count may represent a minor breakthrough from Comet Way to Hatfield PWS caused by movement generated in the Tracer remobilisation. If this was the case this breakthrough would give an apparent flow velocity of approximately 228m/day. It should be noted, that at the time of remobilisation, total numbers of phage in tracer the were relatively low, A recovery of 2pfu/ml, assuming it rises and falls to that concentration over a period of approximately 24 hours at a discharge rate of $6Ml$ would account for approximately 2.4×10^{10} phage, assuming the concentration at re-mobilisation of 7400pfu/ml in the borehole, if it is tracer it would account for about 2% of the borehole tracer at the time of remobilisation.

However, despite exceeding the local background concentration, the sporadic nature of the occurrences and the fact that they are within the likely range of background concentrations when considered regionally it is considered that the occurrences of $\Phi X174$ phage detected at Hatfield PWS are most likely to represent background occurrences of the phage and not breakthrough of tracer from the Comet Way Borehole.

5.10.3.2.2 Turnford PWS At Turnford PWS, none of the $\Phi X174$ detections forms a consistent pattern, all are discrete and separated by long periods of non-detection. No local background samples could be collected from Turnford PWS so it is uncertain what the true background level at that location might be.

Given the sporadic nature of the measured occurrences and the fact that they are within the range of regional background samples it is considered that the occurrences of $\Phi X174$ phage detected at Turnford PWS are most likely to represent background occurrences of the phage and not breakthrough from the Comet Way Borehole.

There appears to be no apparent relation to the re-mobilisation of tracer at Comet Way, there is a possible occurrence of 2pfu/ml at 912 hours, 240 hours after "re-mobilisation" this is slower than a simultaneous spike seen at Amwell Marsh and Lynchmill Spring (see section 5.10.3.3 but might be consistent with longer transport distance.

5.10.3.2.3 Chadwell Spring Only 1 sample from Chadwell Spring tested positive for $\Phi X174$ Bacteriophage, giving a concentration of 1pfu/ml at 916.6 hours after injection and approximately 246 hours after the "remobilisation" at the injection borehole. The magnitude of the breakthrough is well within the likely range of natural background found both regionally and locally.

Based on these data it is tentatively concluded that there was no clear breakthrough of the Comet Way Tracer at Chadwell Spring.

The lack of a breakthrough, even at low levels at Chadwell Spring for any of the 3 phage tracers employed is unusual, especially compared with the results of historic tracer tests of the early 20th century. This issue is discussed further in Section 5.10.5.

5.10.3.2.4 Rye Common None of the three samples analysed at Rye Common contained detectable concentrations of $\Phi X174$, on this basis there is no evidence to suggest a connection to the Comet Way borehole, however the sparseness of data (especially at early times, since Rye Common was not initially selected to be a monitoring location for $PhiX174$ phage) and possibility of a breakthrough below detection limits cannot be ruled out.

5.10.3.2.5 Rye Common None of the three samples analysed at Rye Common contained detectable concentrations of $\Phi X174$, on this basis there is no evidence to suggest a connection to the Comet Way borehole, however the sparseness of data (especially at early times, since Rye Common was not initially selected to be a monitoring location for $PhiX174$ phage) and possibility of a breakthrough below detection limits cannot be ruled out.

5.10.3.3 Consistent Occurrences of $\Phi X174$ phage at Background Levels

As discussed above, the measured concentrations of $\Phi X174$ cannot be easily distinguished from the background levels, both when considered against background samples taken locally and against the likely range of samples when considered regionally. However, this does not preclude the possibility of low levels of tracer being present at concentrations equal to the measured background, especially since the background appears to be variable typically between 0 and 1pfu/ml.

When considered in the context of what is understood from monitoring the tracer source boreholes (see section 5.2) it is apparent that a single instantaneous slug injection of tracer into the aquifer does not a suitable approximation for the release from the Comet Way Borehole. However, the overall pattern is consistent with a slower release of tracer over a longer period of time with tracer being lost from the borehole exponentially as a result of dilution and decay similar to that of a borehole dilution test. An additional complication is that of all the phage species Phi X174 had the lowest overall injection concentration and mass (an order of magnitude less than that of the *Serratia Marcescens* phage) which would result in lower observed concentrations assuming both are transported via a similar transport mechanism.

The general pattern of $\Phi X174$ phage concentrations is similar at a number of observation points; Essendon PWS, Arkley Hole Spring, Lynchmill Spring and Amwell Marsh PWS, and comprises a series of short duration breakthroughs or peaks of $\Phi X174$ concentration decreasing in size with time, preceded and followed by relatively long periods of non-detection. Temporarily ignoring the presence of the

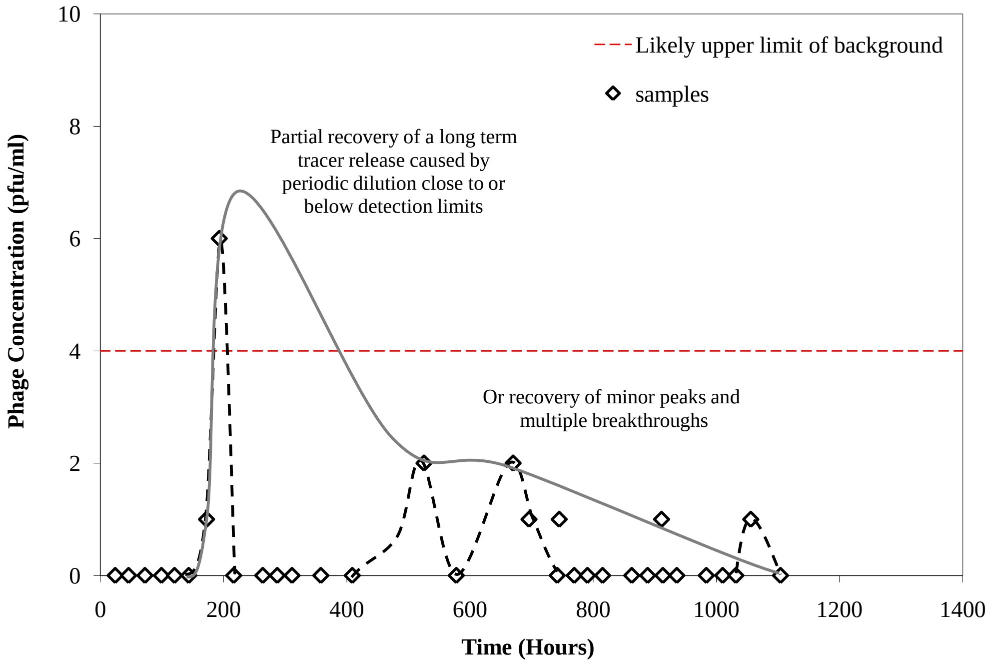


Figure 5.27: Possible mechanisms of $\Phi X174$ breakthrough assuming the occurrences are those of tracer and not background

background and assuming that all occurrences at these locations are due to breakthrough of tracer two possible models are proposed.

1. Coupling the likely tracer release with the likely transport mechanisms within a discrete and perhaps karstic fracture and conduit network with a variety of flow paths and speeds as, and factoring in environmental effects which could impact flux from the injection borehole could have resulted in a discrete series of breakthroughs representing different flow paths and or pulses of tracer release from the injection borehole, the overall concentration of which diminishes with time as the source is diluted and/or inactivated.

2. A possible alternative explanation for the form of the data, given the close proximity to detection limits is that that the discontinuous detections of might define a single dispersed breakthrough of a tracer pulse however periodic dilutions and/or variations in tracer flux from the borehole (for example by recharge events) and analytical errors may have reduced concentrations below the detection limit and therefore a full continuous breakthrough curve might not be observed.

These possible conceptual models of breakthrough are illustrated in figure 5.27 using the occurrences of $\Phi X174$ at Essendon PWS as an example.

5.10.3.3.1 Staggered Observations of $\Phi X174$ Tracer If either case were correct, the release of tracer would create a pulse or several pulses of tracer that migrate downgradient from the injection borehole and would appear to be staggered in time

Table 5.21: Staggered Observations of $\Phi X174$ Phage

Peak	Peak Times (Hours after injection)	Location	Consecutive Sample Concentrations (pfu/ml)
A	172.3 - 192.9	Essendon PWS	0,1,6,0
	216.5 - 264.7	Arkley Hole Spring	0,3,1,1,0
	215.2 - 312.8	Lynchmill Spring	0,1,3,4,1,0
B	578.2	Arkley Hole Spring	0,1,0
	601.76 - 625.77	Lynchmill Spring	0,1,2,1,0
C	744.8	Essendon PWS	0,1,0
	791.12	Lynchmill Spring	0,1,0

and distance from the Tracer injection borehole, a pattern that might be expected should the tracer be moving in a progressive pulse downgradient from the tracer source. Table 5.21 indicates possible staggered observations in the data listed in order of occurrence and distance from injection borehole.

The occurrence of $\Phi X174$ at Essendon, Arkley Hole and Lynchmill Spring between 172.3 - 312.78 hours after injection (Peak A) shows a number of characteristics that are consistent with what is likely to be observed if this were a pulse of tracer moving progressively downgradient to each location and this series of occurrences is considered to be the most likely candidate for breakthrough of $\Phi X174$ phage tracer rather than background variations.

- The sequence includes the highest occurrence of $\Phi X174$ recorded, 6pfu/ml, outside the background range at Essendon PWS
- The measured peak concentrations appear to decrease with distance (although Lynchmill Spring does show a higher concentration than Arkley Hole)
- The spread of observations increases with distance from Comet Way suggesting it could be dispersing in a downgradient direction
- The staggered arrival follows the same pattern of arrival, including near simultaneous arrival at Lynchmill Spring and Arkley Hole, as for a secondary peak of *Serratia Marcescens* phage tracer; reaching Essendon PWS (140.1 hours) Arkley Hole (189.2 hours) and Lynchmill Spring (185 hours)

If the apparent breakthrough from Comet Way is following a straight line due east along the Palaeocene feather edge to Essendon PWS, Arkley Hole and Lynchmill Spring this would suggest flow velocities of 786m/day to Essendon, 809m/day to Arkley Hole and 1779.2m/day to Lynchmill Spring for the initial breakthrough and 702.9m/day, 809m/day and 1327m/day for Essendon PWS, Arkley Hole and Lynchmill Spring respectively for the peak breakthrough.

Heavy rainfall (20mm in 3 days) occurred between 113 and 178 hours following injection, just prior to this sequential detection and it is possible it is related, either by mobilising the tracer from the vicinity of the injection borehole or by increasing

Table 5.22: Simultaneous Observations of $\Phi X174$ phage

Peak	Peak Times (Hours after injection)	Location	Consecutive Sample Concentrations (pfu/ml)
D	336.7 - 361.0	Arkley Hole Spring	0,2,1,0
	336.3 - 527.5	Amwell Marsh PWS	0,1,2,1,0
E	434.8	Arkley Hole Spring	0,1,0
	432.2 - 456.2	Lynchmill Spring	0,2,3,0
F	525.4	Essendon PWS	0,2,0
	528.2	Lynchmill Spring	0,2,0
G	669.9 - 695.8	Essendon PWS	0,2,1,0
	673.8 - 697.25	Lynchmill Spring	0,1,2,0
H	866.8 - 888.2	Amwell Marsh PWS	0,3,3,0
	863 - 888	Lynchmill Spring	0,4,4,1,0
I	910.9	Essendon PWS	0,1,0
	912.4	Lynchmill Spring	0,1,0

regional background concentrations which could also be responsible for the apparent observations.

Two other staggered observations occur, however, given the lower overall concentrations and lack of any supporting circumstantial evidence, it is more difficult to justify these as likely tracer occurrences as opposed to co-incidental background counts. However both occasions indicate downgradient increase in travel time, the relative timing of which, is broadly consistent (Arkley Hole - Lynchmill spring $\approx 20-50$ hours and Essendon - Lynchmill Spring ≈ 45 hours) with that of the likely breakthrough of $\Phi X174$ and that of *Serratia Marcescens* phage.

5.10.3.3.2 Simultaneous Occurrences of $\Phi X174$ Table 5.22 indicates simultaneous or overlapping occurrences of measured $\Phi X174$ phage at locations where phage counts were measured at background levels at similar times or within the length of one sampling interval, usually of around 24 hours.

Near simultaneous timing of phage counts at similar levels above detection limits occur most commonly at spring sites but also at Essendon PWS and Amwell Marsh. The simultaneous arrival of phage at locations at different distances from the tracer source (e.g. Essendon and Lynchmill Spring) would probably require one of the following conceptual mechanisms.

- A regional (non local) background source that is activated or transported by a regional mechanism, for example rainfall and run-off.
- Transport from a single source (e.g. the tracer borehole) via different transport routes of differing travel times
- Or these occurrences are un-related and the timing is coincidental due to a noisy background

Heavy rainfall events that might account for higher regional background counts occur between 113 - 178 hours, 234 - 324 hours and 1319 - 1400 hours after tracer injection. If these are adjusted by the lag times of correlation with rainfall indicated by the statistical analysis in Section 5.4.1.1 ($\approx$ 48 hours at Essendon, $\approx$ 72 hours at Arkley Hole, $\approx$ 96 hours at Amwell Marsh and $\approx$ 144 hours at Lynchmill Spring) this could indicate that the simultaneous observation at Amwell Marsh and Arkley Hole between 336 and 527 hours could be related to rainfall however none of the rest show any correlation with heavy rainfall, although they may correlate with smaller rainfall events. None of these correlated breakthroughs occur between Arkley Hole and Essendon PWS which are relatively close to each other and show similar patterns of both bromate and *Serratia Marcescens* phage concentration.

Of the occurrences outlined above, the strongest possibility of a breakthrough of tracer is for peak H, the occurrence of phage at moderately high levels (relative to other measurements) between 863 and 888 hours after injection at Amwell Marsh and Lynchmill Spring. Both locations are positioned at similar distance and position almost due east from Comet Way at 16.2km and 15.9km respectively. In addition, both of these occurrences are at higher concentrations than usually observed (at the highest recorded background) at these locations and are consistent over in two samples over a 24 hour period. The sampling followed a relatively dry spell with only 10mm recorded over the in the preceding 12 days which reduces the likelihood of this occurrence being related to rainfall.

In addition, these phage occurrences are approximately 194 - 216 hours after re-mobilisation of the comet way borehole. It is possible that these increased concentrations of phage might have resulted from tracer being mobilised during this procedure and migrating to these discharge points in the Lee Valley.

If these breakthroughs are actually tracer, this would imply a straight line flow velocity and connection with the Comet Way borehole of around 449 m/day for Amwell Marsh PWS after the initial injection or 2007m/day if the breakthrough is a result of the remobilisation, this is broadly consistent with travel times derived for Amwell Marsh PWS for *Serratia Marcescens* ($\approx$ 2400m/day). At Lynchmill Spring, this would result in a straight line connection and flow velocity of around 444m/day for Lynchmill Spring or 2005m/day if this occurred as a result of the remobilisation. These data would imply a karstic connection between the Hatfield Area and the Lee Valley that might be slightly slower than that of the Water End - Lee Valley flow system

This consistency of the travel times and flow velocities would appear to imply a similar transport mechanism, although the lateral distance between the sites (approximately 3.8km) must imply that this transport pathway diverges. Evidence exists that could suggest that this is, at least in part, a background occurrence since it is correlated with occurrences of moderate concentrations of $MS2$ phage at both locations, which is characteristic of some of the background samples.

Table 5.23: Single observations of $\Phi X174$ phage

Times (Hours after injection)	Location	Sample Concentrations (pfu/ml)
87.8 - 95.8	Arkley Hole Spring	1, 1
164.3	Lynchmill Spring	2
719.3	Arkley Hole	1
984 - 1008	Lynchmill spring	1, 1
1055.8	Essendon PWS	1
1199.8	Lynchmill spring	1
1247.8	Lynchmill spring	1
1321.7	Arkley Hole	1

5.10.3.3.3 Single Observations A number of single un-correlated observations of $\Phi X174$ phage also occurred, however these are more difficult to determine since there is no supporting evidence to delineate them from background occurrences.

Given that all of these samples are dominantly concentrations of 1pfu/ml and in generally occur at late times it is most likely that they probably represent sporadic background occurrences.

5.10.3.4 Recovery of $\Phi X714$ phage

Estimating recovery of the $\Phi X174$ phage is complicated by the difficulty in distinguishing tracer breakthroughs from background occurrences. For example, if recovery was calculated for all occurrences of $\Phi X174$ phage at Amwell Marsh PWS using the same methods and assumptions used to calculate recovery of *Serratia Marcescens* then the total recovery of $\Phi X174$ is estimated to be 1.37×10^{15}pfu), an order of magnitude greater than the actual number of phage injected (4×10^{14}pfu). There must therefore be a background contribution to the occurrence of $\Phi X174$ phage.

The estimate for $\Phi X174$ tracer recovery must therefore be based only upon the occurrences which are considered most likely to be tracer breakthroughs, of these there are two principal occurrences:

1. The staggered occurrence of phage at Essendon, Arkley Hole and Lynchmill spring between 172 and 312 hours after injection

2. The simultaneous arrival at Amwell Marsh PWS and Lynchmill Spring between 866 and 888 hours either as a result of slow migration or due to the borehole re-mobilisation.

These breakthroughs are presented on Figure 5.28, for clarity, all other data for these locations are not plotted

A further consideration in considering the recovery of $\Phi X174$ is defining the proportion of these breakthroughs which may be due to background contribution of phage (since this can range from 0 to 4pfu/ml.) In calculating recovery a background of 0pfu/ml has been assumed, i.e. that all of the suspected peaks is due to

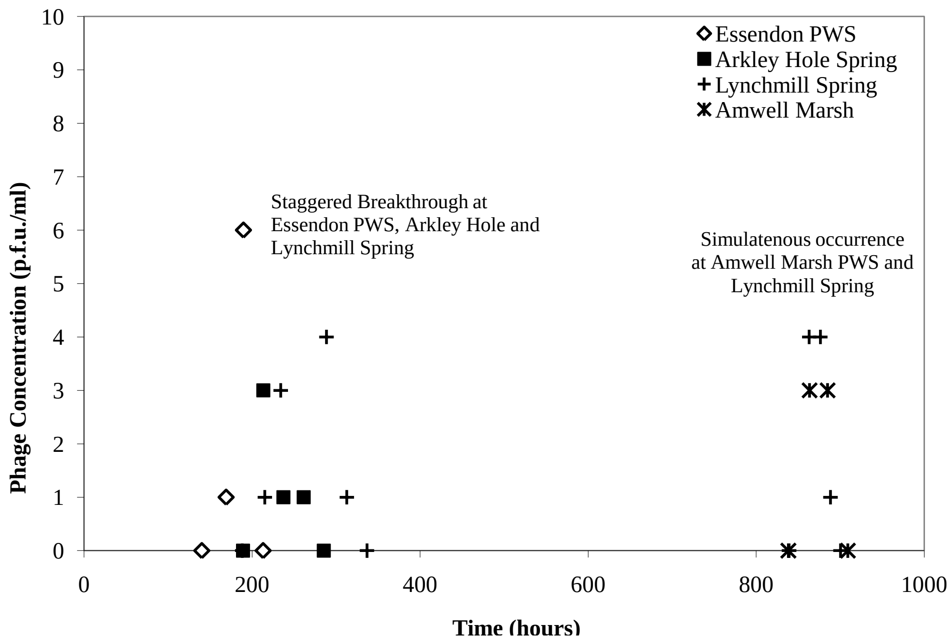


Figure 5.28: Possible breakthroughs of $\Phi X174$ phage

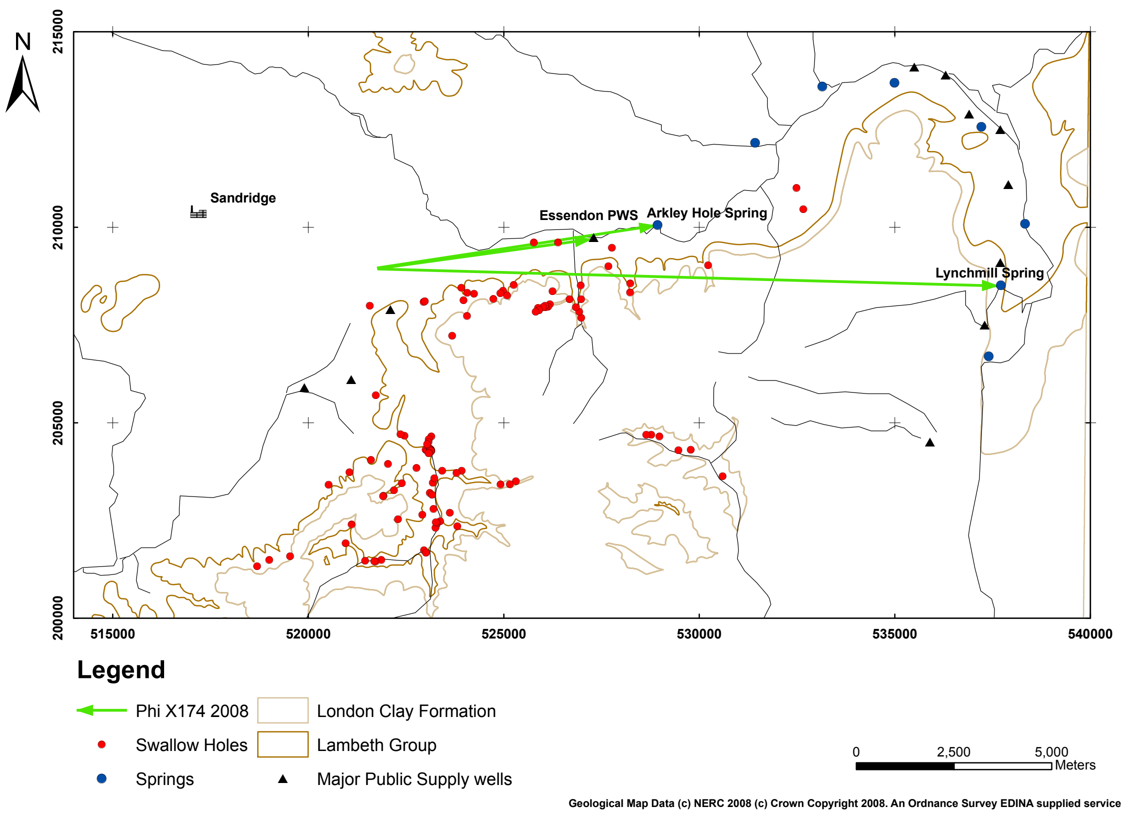


Figure 5.29: Locations at which $\Phi X174$ tracer breakthroughs are suspected

Table 5.24: Estimated recovery of $\Phi X174$ from the suspected phage breakthrough candidates. * Aquifer mass is estimated as that available subtracting the estimate of mass remaining in the borehole (see Section 5.6)

Breakthrough	Location	Recovery (pfu)	% of Mass Recovered Injection	Available	In aquifer*
Staggered Arrival	Essendon PWS	4.50×10^{11}	0.11%	1.69%	5.62%
	Arkley Hole	1.25×10^{12}	0.32%	8.57%	15.61%
	Lynchmill Spring	1.40×10^{12}	0.47%	16.8%	17.44%
	Total	3.1×10^{12}	0.77%	26.98%	38.7%
Simultaneous Arrival	Lynchmill Spring	2.47×10^{11}	0.06%	7665%	
	Amwell Marsh PWS	4.68×10^{13}	11.7%	1595162%	
	Total	$4.71 \times 10^{1}3$	11.76%	1602826%	

tracer, however it may be that some unknown proportion (which cannot be reliably estimated except perhaps for the occurrence outside the background range at Essendon) is due to a background contribution so that the actual proportion of tracer could be as little as 1pfu/ml in each sample. If this is the case, as might be likely this would tend to over-estimate the amount of tracer recovered.

Based upon these breakthroughs, and using the trapezoid method, the estimated recovery at these locations is presented in Table 10.11 expressed both as a percentage of the total injection mass and the total available tracer correcting for decay based upon an inactivation rate of $0.14log_{10}$ per day (Gerba et al., 1991) and as a percentage of the total available phage that had left the borehole at the time of recovery.

If the staggered breakthrough is genuine, it represents a large recovery of the available mass of tracer despite the low overall magnitude of concentrations and is therefore consistent with a slow release mechanism and lower overall injection titre compared with the other tracers.

If the recovery assumptions (see Section 5.10.2) are appropriate, the simultaneous late arrival of $\Phi X174$ at Lynchmill Spring and Amwell Marsh would represent a recovery far in excess of the total active tracer within the aquifer due to the high numbers of phage estimated to be recovered at Amwell Marsh PWS.

Recovery estimates can therefore be used to improve the veracity of a genuine breakthrough of this tracer injection and would suggest in this case that whilst the earlier breakthrough to Essendon PWS, Arkley Hole and Lynchmill Spring may be consistent with a tracer occurrence, the later simultaneous arrival at Lynchmill Spring and Amwell Marsh, which would appear to give a strong visual correlation suggestive of a breakthrough may actually be background or the assumptions used to estimate recovery are inappropriate, for example, the duration of tracer arrival may be shorter than the width of the sampling interval used in the trapezoidal method, the assumed inactivation rate is too high for $\Phi X174$ under the conditions in this tracer test. That it is a background occurrence, and not tracer, is further be supported by the occurrence of moderately high $MS2$ phage in two of these samples.

5.10.4 Discussion of $MS2$ Phage Results

As with $\Phi X174$ phage, delineating $MS2$ tracer occurrences from background of $MS2$ are complicated by their proximity to detection limits and background concentrations of the samples. Of the $MS2$ Samples, only 2 samples gave $MS2$ concentrations outside the likely range of the regionally determined background

- A sample concentration of 8pfu/ml in the New River downstream of Amwell Marsh at 190.8 hours after injection
- A sample concentration of 8pfu/ml at Hatfield Quarry Observation Borehole WM12 at 746.43 hours after injection

The New River sample was the first detection of $MS2$ phage outside the background range, however, a number of features of this occurrence shed doubt on it being a genuine breakthrough of $MS2$ tracer.

- The sample also contains high $\Phi X174$ (4pfu/ml) a feature characteristic of relatively high background occurrences of both phage.
- The New river appears to have relatively high concentrations of both $MS2$ and $\Phi X174$ phage when compared to groundwater locations and the background concentrations in the river may be higher than that determined from groundwater locations (No background samples were collected from the New River).
- The sample was preceded by heavy rain between the 8th - 10th March 2008 which is linked to occurrences of high background.
- At the distance of Amwell Marsh PWS from the tracer injection point ($\approx$ 20km) the apparent straight line velocity of this breakthrough would be $\approx$ 2.5km/day, this is consistent with other karstic speeds identified in this investigation but is unusual in that the occurrence was isolated to the new River and not detected at any other locations, especially those located closer to the injection point such as Hatfield PWS and Essendon PWS, or the springs at Arkley Hole and Lynchmill which might have a stronger connection to the karst system.
- Although the sample was taken close to the discharge point of Amwell Marsh PWS, it is not known to what extent the sample reflects discharge from the abstraction well rather than concentrations in the New River. It is possible that this could reflect New River concentrations which are itself derived from the River Lee where background may be higher or could have carried effluent discharge of tracer containing groundwater to the location at faster velocity than the groundwater.

Table 5.25: Occurrences of $MS2$ phage above 1pfu/ml

Times (Hours after injection)	Location	Sample Concentrations (pfu/ml)
262.2 - 285.7	Essendon PWS	0,1, 2,0
311.3 - 335.3	Arkley Hole	0,1, 3,0
407.5 - 694.4	Essendon PWS	0,1,1,2,1,0
552.8 - 576.8	Arkley Hole Spring	0,2,1,0
861.75	Lynchmill Spring	0,4,0
1246.4 - 1318.4 Lynchmill Spring	0,1, 2, 1, 2,0	

The occurrence at Hatfield Quarry WM12 is probably the most likely single occurrence of $MS2$ phage likely to be tracer, it comprises a single occurrence of 8pfu/ml. Hatfield Quarry Borehole WM12 is located in approximately the centre-line of the Bromate Plume at a location of relatively high bromate concentrations and is thus considered to be located close to the main area of bromate migration, as was Harefield House. Occurrence of $MS2$ here is well outside the background range determined for all locations within the Vale of St Albans (the highest concentration being 2pfu/ml). Unfortunately due to the relatively infrequent sampling regime no samples were taken prior to this sample for approximately 300 hours, however the sample taken following this detection (120 hours later) also contained a $MS2$ phage concentration of 1pfu/ml.

If this is a genuine occurrence of tracer it would indicate an apparent straight line velocity of approximately 55m/day much slower than the karstic flows indicated further east and possibly more consistent with non-karstic fracture flow in the Chalk (e.g. Price et al., 1992).

5.10.4.1 Other Occurrences of $MS2$ phage

If it is assumed that a background concentration of 1pfu/ml $MS2$ phage should be expected at most locations and that this background eliminates considerations any occurrence of $MS2$ phage at 1pfu/ml that are sporadic and non-consecutive as background concentrations then, as with $\Phi X174$ the remaining occurrences should be considered in terms of the consistency, timing and pattern of their arrival to see if they can be delineated from background concentrations. These occurrences for all locations are presented in Table 5.25.

Of these occurrences, the sample of 2pfu/ml 668.6 hours at Essendon PWS, the sample of 3pfu/ml at Arkley Hole after 335.3 hours and the sample of 4pfu/ml at Lynchmill Spring after 861.75 hours are accompanied by occurrences of $\Phi X174$ phage in the same sample, which could be indicative of background occurrences. If these are eliminated as potential tracer occurrences then the measured concentrations of $\Phi X174$ at Essendon at between 262.2 and 285.7 hours, at Arkley Hole between 552.8 and 576.8 hours, and at Lynchmill Spring between 1246 and 1318 hours remain possible candidates for breakthroughs. These are presented in figure 5.30, all other data from these locations has been omitted for clarity.

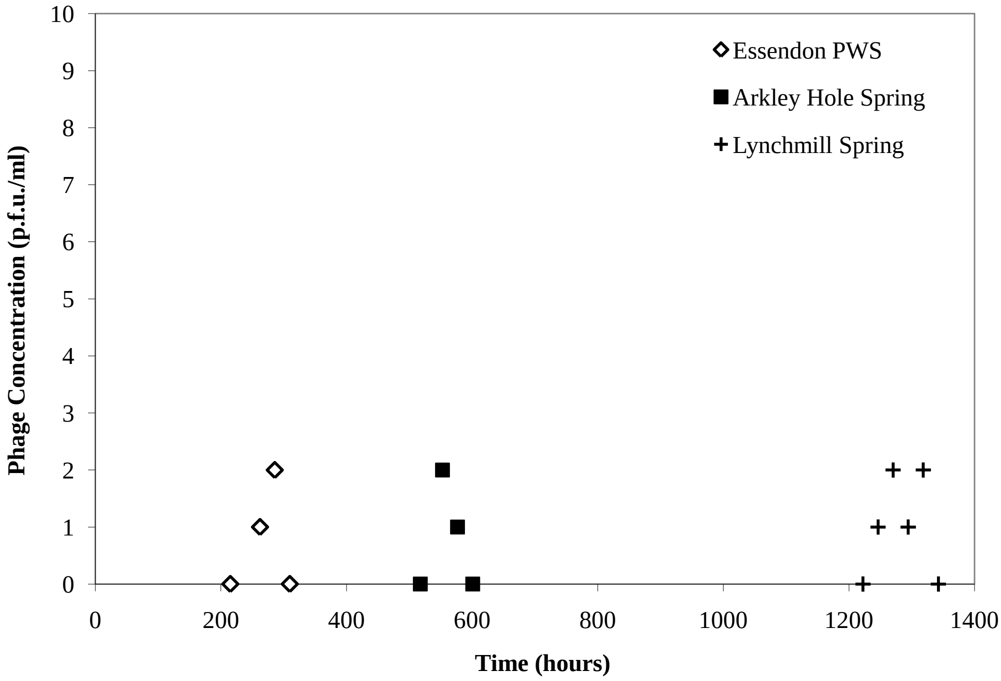


Figure 5.30: Possible breakthroughs of $MS2$ phage

Heavy rain does occur between 230 - 300 hours and might account for the occurrence at Essendon between 262 and 285 hours but rainfall events do not correlate well with the other occurrences of the $MS2$ phage.

The relative arrival times of these occurrences is consistent with a downgradient migration of a pulse of tracer from the injection point, although the relative travel times are much longer than has been inferred for *Serratia Marcescens* and $\Phi X174$ phage.

If these travel times are converted to straight line velocities this would give first and peak arrival travel times of 877m/day and 805m/day for Essendon PWS, 487m/day for Arkley Hole and 386m/day and 376m/day for Lynchmill Spring. These speeds are much slower than that indicated for the karstic flow from Water End and possibly from Comet Way but perhaps are consistent with slower fissure dominated or semi-karstic flow perhaps developed in the partially eroded Palaeo-karst that might be present in the Vale of St Albans.

Comparing the relative timing of this potential breakthrough for the locations east of Hatfield (Essendon PWS, Arkley Hole and Lynchmill Spring) with the timing of the potential breakthrough at Hatfield Quarry (at 746 hours after injection) would suggest that if genuine, the occurrence at Essendon PWS and Arkley Hole is independent of this flow path and may have rapidly by-passed the monitoring locations in the Vale of St Albans.

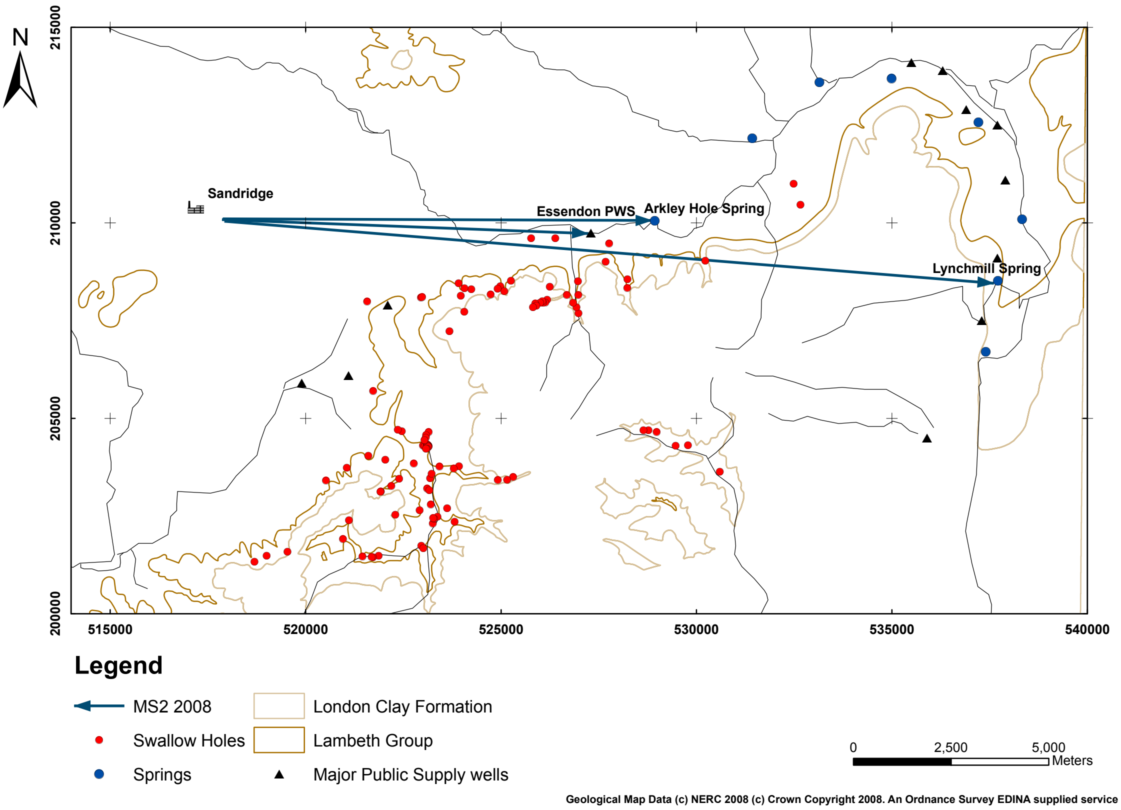


Figure 5.31: Distribution of possible breakthroughs of $MS2$ tracer

Table 5.26: Recovery of $MS2$ phage from suspected breakthroughs. * Aquifer mass is estimated as that available subtracting the estimate of mass remaining in the borehole (see section 5.6)

Location	Recovery (pfu) (pfu)	% of Mass Recovered Injection	Available	In aquifer*
Essendon PWS	3.034×10^{11}	0.00101%	0.0025%	0.0027%
Arkley Hole	8.69×10^{11}	0.00289%	0.0088%	0.0097%
Lynchmill Spring	3.372×10^{11}	0.00124%	0.076%	0.087%
Total	1.11×10^{12}	0.0052%	0.096%	0.109%

5.10.4.2 Recovery of $MS2$

Of these occurrences at Essendon PWS, Arkley Hole and Lynchmill Spring, it is possible to make an estimate of the phage recovery using the same methods for *Serratia Marcescens* and $\Phi X174$ phage. This is compared with both total injected phage and the available phage (i.e. that has left the injection borehole and not decayed) and is presented in table 5.26. The breakthrough of phage at Hatfield Quarry WM12 is not included since it is not an active abstraction well and hence the recovery from this location is negligible.

The apparent overall recovery for $MS2$ is much lower than for the other two phage species, in part this is likely to be due to comparing recovery (with is 1-2 orders of magnitude lower than for other phage) with much higher injection titre (1-2 orders of magnitude greater).

It may also suggest that there is greater dispersion of the $MS2$ tracer compared with the other injections, either as an influence of dilution or by dispersion of the tracer pulse, a proportion of which might be dual porosity related given that it is assumed to dominate within the Vale of St Albans.

This karstic/semi-karstic bypass may represent only a very minor proportion of the transport of tracer within the Vale of St Albans, however it may be important when considered in the context of Bromate since it suggests there is some, albeit weak evidence for a rapid bypass from the Vale of St Albans to at least Essendon PWS and possibly directly to the Lee Valley.

5.10.5 Chadwell Spring

Of the 18 samples collected from Chadwell Spring, none of any of the phage species were detected at concentrations in excess of the regionally or locally established background levels and most analyses indicated phage were below detection limits.

The discharge pool for Chadwell Spring is large and deep being approximately 30m in diameter and $3m$ deep and visual observations prior to and during tracing did not identify any discrete upwellings into the pool. Chadwell Spring was sampled from the most easily accessible place, from the neck of the discharge channel so that a representative sample of the spring water leaving the discharge pool was obtained.

Chadwell Spring was discharging over the outflow weir at all times during the test. The estimated observed discharge ranged from a minimum of $\leq$ 5l/s but was typically around $10-15$l/s and was estimated to reach $20-30l/s$ at the maximum observed discharge. This gives a typical daily discharge in average of $0.8-1.2$Ml/day on days which it was observed but a maximum daily discharge has been measured at over 4Ml/day (Newton, 2005b).

If this discharge volume is compared to the estimated volume of the discharge pool ($0.7Ml$ assuming a 3m deep, 30m diameter conical pool) it would indicate a residence time within the pool of 14-24 hours at normal flow rates if inflows and outflows are equal.

The degree of mixing within the discharge pool is unknown, if it is limited and the residence time of incoming water is large it is possible that any occurrence of tracer, especially if it were at low concentrations may either been diluted, sorbed or inactivated beyond detectable limits prior to sampling, thus preventing detection of any tracer at this location. In addition to dilution, longer residence would also lead to more exposure of the tracer to UV light and rainfall which would cause further dilution and exposure to organic matter (plants and animal waste) which may have increased sorption.

Abstractions in TWUL's NNR well-field influence discharge at Chadwell Spring and the Emma's Well Spring (Whittaker, 1921) and it is possible that tracer that might otherwise arrived at Chadwell Spring was intercepted and recovered at nearby abstraction wells. Of the wells close to Chadwell Spring, only Amwell Marsh PWS and Rye Common PWS (both of which discharged tracer) were in continuous operation at high discharge rates during the tracer testing. Closer wells to the spring, which could be more likely to have a stronger influence such as Broadmeads PWS, Amwell End PWS and Amwell Hill PWS were not operating, although as suggested above, proximity does not necessarily imply connectivity when considering a karstic flow system.

(Assem, 2005) suggested that water chemistry of the Chadwell spring discharge is distinct from that at other major springs nearby (e.g. Arkley Hole and Lynchmill Spring) with a higher concentration of elements that were indicative of longer residence time groundwater derived from distant and diffuse recharge to the Chalk, rather than the chemistry more typical of the Mymmshall Brook surface water that was observed at Arkley Hole and Lynchmill Spring.

It has been suggested that Chadwell Spring draws more water from the North of the River Lee rather than the south and south west and the Water End System. The present study would appear to partially support such a hypothesis with the occurrence of all species of phage at Chadwell Spring being distinct from that recorded at Arkley Hole and Lynchmill Spring which were broadly similar.

If this is the case if would also suggest that this change has occurred, probably as a response to changing abstraction and dewatering of the aquifer since the 1930's when tracing from Water End identified a strong connection between Water End and Chadwell Spring.

5.10.6 $\Phi X174$ and $MS2$ Phage in the New River

Both $MS2$ and $\Phi X174$ phage appear to be relatively common at concentrations in the range of regionally established background levels within the New River. A detailed comparative analysis of these data is made more difficult by the relatively sacristy of data for the New River locations, however when the data available are compared with the borehole locations or other groundwater discharges, for example at Arkley Hole and Lynchmill Spring, the occurrence of the phage at detectable concentrations appears to be more frequent in the New River.

Two samples from the New River gave phage concentrations outside the background range of phage.

- A sample taken from the New River downstream of Amwell Marsh PWS gave a $MS2$ phage concentration of 8pfu/ml (and a $\Phi X174$ concentration of 4pfu/ml) 190.8 hours after injection of the $MS2$ phage compared with a background of $1 - 4$pfu/ml

- A sample from the New River taken from Kings Meads at 1225 hours after injection for $\Phi X174$ does provide a phage concentration in excess of the regionally determined background (5pfu/ml compared with a background range of $0 - 4$pfu/ml, but is not outside the likely statistical range)

Despite being outside the regional background as determined for groundwater discharge locations, a background was not established for the New River since at the time of designing the original sampling regime collection of samples from the New River was not envisaged and so no data are available to determine if the New River might have a larger background range than the groundwater sites and may represent a higher fluctuation than previously seen. That phage appear to be more common at higher concentrations ($3-4$pfu/ml) in the New River compared to groundwater discharges at least suggest that this is possible. Also of consideration is that for $MS2$ a relatively high concentration of $\Phi X174$ was also recorded, which is characteristic of some background samples).

The high count of $\Phi X174$ at Broadmeads is not correlated with high concentrations of $\Phi X174$ or $MS2$ phage at any other New River Location. Given the high volume of flow in the New River (up to 220Ml/day) there is likely to be a high degree of dilution of any phage entering the system and apparent low concentrations actually represent large numbers of phage.

The bulk of the flow of the New River is derived from diversion of the River Lee at New Gauge west of Kings Mead and Chadwell Spring. The New River also receives a contribution of groundwater from Chadwell Spring and output from TWUL Northern New River Wells, amounting to approximately 35Ml/day during the tracer test as well as input from wells further to the south. During the tracer testing the flow of the River Lee diverted into the New River at New Gauge was approximately 100Ml/day, Based on this discharge the phage concentration measured would be equivalent to $2-5\times10^{11}$pfu/day. When this is compared with the amount of $\Phi X174$ tracer likely to be left active at this time (based upon the decay figures previously adopted) there could be over 10,000 times as many phage in the New River as were left active from the tracer injection into the aquifer at this time after injection.

On this basis it is concluded that although these two samples that fall outside the background range established for groundwater are more likely to represent high background occurrences rather than true tracer breakthroughs to the New River and that high background occurrences are characteristic of the New River.

Since the bulk of the New River's flow is derived from surface water of the River Lee, it possible that much of detection comprises background run-off to the river is likely to result in contamination with organic plant and animal matter, including faecal material and wastewater (e.g. from WTW outfalls) which might contain the phage or their host bacteria such as E-coli and other Enter-bacteria and hence there may either be low level production of the phage in the environment, or persistence of phage at low concentrations.

If this is the case it is uncertain why the measured background occurrence of both phage is not more ubiquitous and consistent, both with time and spatially

Table 5.27: Selected Correlation Coefficients with rainfall and turbidity for Essendon PWS

parameter	Days Lag on Rainfall				Turbidity
	0	1	2	3	
$MS2$ phage	0.219	-0.244	0.0161	0.320	0.0804
$\Phi X174$ phage	0.0156	0.398	0.353	-0.0130	0.0301
Turbidity	-0.192	0.0117	0.669	0.285	-

between locations, and not as variable as seen in the sample regime (even allowing for $\pm 20\%$ analytical error, which amounts to < 1pfu/ml at these concentrations).

In groundwater sources, the potential for wastewater, sewage or organic matter sources are likely to be less common and will not be directly linked to the groundwater system. There is also likely to be some natural attenuation especially in the unsaturated and soil zones where phage adsorption might occur. This could account for the differences in the frequency of occurrence between Groundwater sources and the New River, which is primarily a surface water source with some groundwater component and entirely groundwater derived locations.

Above New Gauge, The River Lee itself derives water from surface run-off, baseflow from Groundwater where it is effluent south of Lemsford (Atkins Reference) and discharge from Springs, such as Arkley Hole and other springs. Since this contains a groundwater component, it is possible that in addition to natural sources, the phage in the New River could potentially contain a proportion of phage tracer that is present in the groundwater that has entered the New River either discretely via springs and abstraction discharges or more diffusely via baseflow along the length of the River Lee. However, it is not possible to identify if this is the actual case and if so, the relative proportions of the sources of $\Phi X174$.

5.10.7 Variation of Phage Concentrations with Rainfall and Turbidity

Correlation between high turbidity, rainfall and the $MS2$ and $\Phi X174$ measurements may help to distinguish between background occurrences and those which might arise due to migration of tracer. However, since the two phage sources cannot be distinguished, it is also possible that recharge events might also impact the tracer source boreholes and the movement of phage within the aquifer for example by causing additional mobilisation of tracer from the borehole.

Figure 5.7 indicates a correlation plot of Turbidity and phage concentration recorded at Essendon PWS, the Pearson correlation coefficients are presented in Table 5.27.

The strongest correlations indicated by this analysis indicate a possible relationship between turbidity and rainfall for a two day lag and also between $\Phi X174$ and $MS2$ phage concentration with rainfall with a 1 day lag. Neither $\Phi X174$ or $MS2$ phage show a strong relationship with turbidity at Essendon PWS, both give

Table 5.28: Pearsons correlation coefficients (r^2 values) of sampled $\Phi X174$ concentrations and daily rainfall at various lag times

Location	Days lag on rainfall							
	0	1	2	3	4	5	6	7
Essendon PWS	0.019	0.289	0.596	0.033	0.008	0.043	-0.121	-0.192
Arkley, Hole	-0.176	0.071	0.432	0.455	0.176	-0.025	0.115	0.186
Lynchmill Spring	0.279	0.091	0.128	0.042	0.083	0.135	0.287	0.115
Amwell Marsh	-0.223	-0.268	0.028	-0.044	0.345	-0.034	-0.111	-0.008
New River at Amwell Marsh	0.098	0.435	0.504	0.302	-0.186	-0.196	0.351	0.428
New River at Kings Mead	-0.215	-0.163	-0.151	0.023	-0.126	-0.585	-0.38	-0.356
New River at Emma's Well	-0.152	-0.417	-0.567	-0.761	-0.178	0.271	0.342	0.081

Table 5.29: Pearson's correlation coefficients (r^2 values) of sampled $MS2$ phage concentrations and daily rainfall at various lag times

Location	Days lag on rainfall							
	0	1	2	3	4	5	6	7
Essendon PWS	0.219	-0.270	-0.124	-0.019	0.444	0.693	0.419	-0.023
Arkley, Hole	0.089	0.114	0.309	-0.084	0.092	-0.012	0.273	0.316
Lynchmill Spring	0.084	-0.097	-0.112	-0.076	-0.130	0.059	-0.066	-0.123
Amwell Marsh	-0.171	-0.145	0.241	-0.005	0.102	-0.103	-0.012	0.322
New River at Amwell Marsh	-0.068	0.891	0.889	0.217	-0.407	-0.315	-0.333	0.040
New River at Kings Mead	0.166	-0.153	-0.324	0.075	-0.035	-0.444	-0.415	-0.308
New River at Emma's Well	0.028	0.697	0.092	0.033	0.672	0.059	-0.492	-0.493

liner correlation coefficients < 0.1 (as does *Serratia Marcescens.*) Based on these data, turbidity probably cannot be used as a proxy for indicating high background concentrations of phage.

However, weak relationships between rainfall and concentrations of $MS2$ and phi x 174 and phage are indicated suggesting that there may be some influence on measured phage concentrations following rain-fall events. Possibly by mobilising phage from source boreholes, flushing of fractures or some other factor. The lack of correlation of phage with turbidity might suggest that phage background variations may not be due to rainfall entering the karst flow system, since the activity of swallow holes at Water End has been linked to high turbidity and bacterial concentrations.

The difference in lag times indicated between correlation of phage with rainfall may indicate a different mechanism of variation, perhaps either indicating a different travel time as a result of increased advection time and distance, which might indicating a different source or could also arise due to relative retardation of the two phage species, for example in the soil and unsaturated zone.

Correlation coefficients of $\Phi X174$ phage concentrations with rainfall at various lag times for other locations which have shown frequent occurrences of $\Phi X174$ at various lag times are indicated in table 5.28 and table 5.29.

The data indicate that for most locations where there is a positive correlation between rainfall and phage concentration the lag time is longer for $MS2$ than for $\Phi X174$. This could either suggest a longer transport distance (which is the actual case if tracer is the source of phage) or a differential transport rate (assuming both are derived from a similar background source). In addition for groundwater locations the lag time appears to increase with distance from the tracer source, as might be expected if the correlation is indicating tracer is being flushed in a pulse from the source borehole to downgradient locations

The relationships at the New River are complex. One of the strongest positive correlations for both $\Phi X174$ and $MS2$ phage is for the New River downstream of Amwell Marsh PWS However this strong relationship is not apparent at locations upstream i.e. Emma's Well and King's Mead which show moderately strong negative correlations for $\Phi X174$, Kings Mead also shows a negative correlation for $MS2$ whilst Emma's well shows a positive one.

The lag times at these locations also do not appear to be related to distance downstream It is possible that this might be reflecting the effects of rainfall effects on the variable but comparatively high background concentrations in the New River as indicated in Section 5.10.6 as well as the effect of the groundwater discharge into the New River at Amwell Marsh PWS.

It should be remembered that although these correlations are informative the data used to construct these relationships are not strictly comparable, total daily rainfall is being compared with discrete measurements of phage concentrations, which may vary over the course of a day and, at Essendon PWS, average daily turbidity data which includes an averaging of variation over the course of a day.

5.11 Summary

Drawing together the analysis of results there is strong evidence for *Serratia Marcescens* Breakthrough to a number of locations. Despite the sample concentrations being similar to that the natural background, there is also limited and increasingly uncertain evidence to suggest that breakthrough of $\Phi X174$ and $MS2$ phage also occurred at a number of locations. These connections are summarised in Table 5.30 and presented in figure 5.32. A qualitative measure has been used to provide a comparative estimate of the strength of evidence for each connection, these categorisations are;

- Strong; persistent occurrences above the local and regionally established background levels
- Medium, occurrences of phage equal to or just exceeding the range of the natural background but with supporting circumstantial evidence such as the pattern of occurrence
- Weak, occurrences equal to or within the range of the natural background with minor supporting evidence but less certainty than "medium" occurrences
- None; no evidence to separate measured phage concentrations from natural background occurrences or no positive detections.

Table 5.30: Summary of evidence for possible tracer breakthroughs

Location	Water End		Comet Way		Harefield House	
	Evidence	Velocity (m/day)	Evidence	Velocity (m/day)	Evidence	Velocity (m/day)
Hatfield Quarry WM12	-	-	-	-	Weak	55
Hatfield PWS	Strong	3207	None	-	-	None - -
Essendon PWS	Strong	2362	Medium	702	Weak	805
Arkley Hole Spring	Strong	2832	Medium	809	Weak	487
Amwell Marsh PWS	Strong	2392	Weak	449	None	-
Rye Common PWS	Medium	1854	None	-	None	-
Lynchmill Spring	Strong	3336	Medium	1327	Weak	376
Turnford PWS	Strong	1889	None	-	None	-

These have only been given for locations that have shown connection to at least one phage species, other locations where no evidence of connection to any phage species are not listed in the table but are listed below, since the discharge point of groundwater into the New River cannot be determined, it too has been excluded from this list.

- Coleman Green Lane
- Nashes Farm
- Capps Cottages
- North Mymms PWS - Fairfolds Farm
- Hatfield Quarry WM8
- Hatfield Quarry WM13 - Hatfield Business Park
- Park Street OBH
- Chadwell Spring

The Serratia Marcescens phage were detected at concentrations in excess of the measured background range at 9 of the 12 locations. First detection occurred between 2 and 7 days after injection and indicate rapid groundwater velocities of between 1.8 and 3.9kmday-1. Overall tracer recovery is estimated at approximately 15% of the injected tracer mass. The travel times and distribution are broadly consistent with the 1920's and 1930's tracing however, better data resolution allowed for the observation of breakthrough curves and secondary tracer peaks suggesting multiple arrivals of tracer. In addition, the occurrence of tracer at Hatfield and Turnford suggests that the spatial distribution of groundwater originating from the swallow holes is much wider than was previously known. The pattern of arrival is consistent with progressive migration and dispersion of a pulse of tracer from Water End along the Palaeocene Feather Edge to the Lee Valley.

$\Phi X174$ bacteriophage were detected at 10 of the 12 monitoring locations. Measured concentrations were similar to that of the natural background which makes

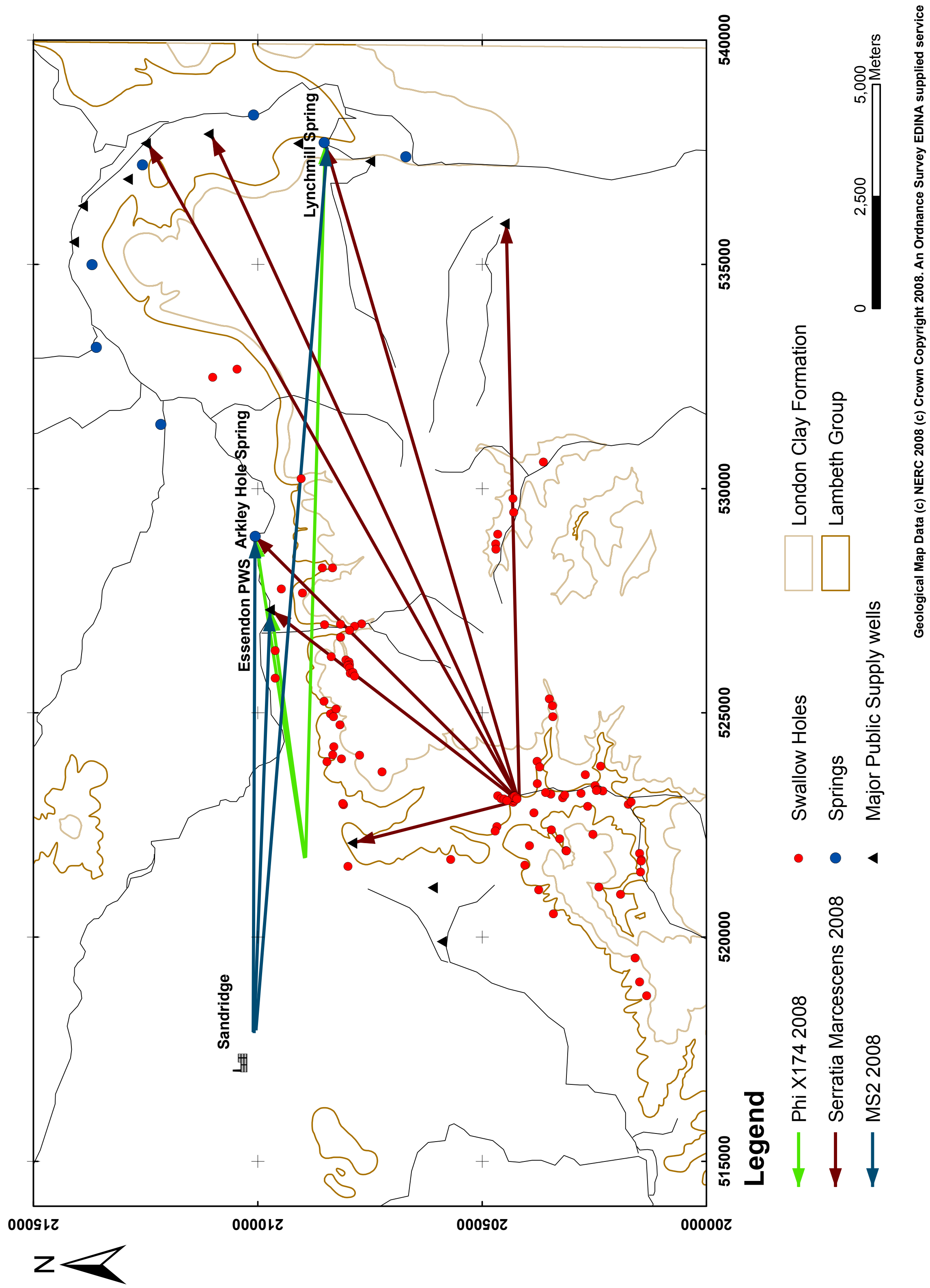


Figure 5.32: Summary of possible and proven connections from the tracer tests

delineation of a clear tracer breakthrough more difficult. However, examination of the data in terms of likely influences on local background concentration such as rainfall and turbidity as well as the consistency of the occurrences and form of the apparent breakthrough curves suggest that there is some evidence to support attenuated breakthroughs at 3 locations; Essendon PWS, Arkley Hole Spring and Lynchmill Spring and suggests a relatively narrow pattern of migration of tracer almost due east along the Palaeocene Feather Edge possibly in a karstic system that may be the same as that of Water End. This would appear to suggest that the karstic system may extend at least as far east as Hatfield and may possibly bypass Hatfield PWS to the north, although the *Serratia Marcescens* phage tracing does indicate that Hatfield PWS is at least connected to the southerly part of the karst system from Water End.

These breakthroughs suggest groundwater velocities between 0.8 and 1.8km/day and overall tracer recovery is estimated at 0.77% of the injection mass. These data are consistent with other tracer test data for semi-karstic chalk (Price et al., 1992; Maurice et al., 2006) in terms of the attenuation of tracer and the overall flow velocities.

$MS2$ Coliphage were detected at 16 of the 19 locations monitored. As with $\Phi X174$ phage, the measured concentrations were similar to that of the natural background, however, in this case there appear to be more frequent sporadic low level occurrences at a wider range of locations and in particular the phage were common in surface waters.

Applying the same methodology as for the Phi X174 phage suggests that there is some evidence for attenuated breakthroughs of MS2 Coliphage tracer at Hatfield Quarry, Essendon PWS, Arkley Hole Spring and Lynchmill Spring. These breakthroughs suggest groundwater velocities between 0.05 and $0.9km/day$.

No tracer, of any species was detected above background concentrations at Chadwell Spring, this could support the findings of which suggest that the spring now derived much of its water from north of the River Lee outside the catchment area of the tracer injections and could suggest that this change has occurred relatively recently possibly as a result of changing abstraction patters in the NNR well-field.

No detections were made at Park Street OBH or North Mymms PWS. For North Mymms PWS, this agrees with findings of the 20th Century test, and could suggest that flow is strongly anisotropic to the North/North East away from Water End, however no sampling was conducted at North Mymms PWS until 3 days into the tracer test so the possibility of a faster connection, especially given the travel time to Hatfield PWS, remains uncertain.

Recovery appears to be correlated with discharge, although despite relatively low discharge rates at spring sites, the recovery is relatively large compared to other locations and is probably indicative of their direct connection to the karstic flow system.

Essendon PWS also appears to have a strong karstic connection, additional evidence for which is provided by high turbidity following rainfall events between which, the apparent lag times agree with the migration times of the *Serratia Marcescens* Phage from Water End.

Large differences in relative arrival times between these locations for all three phage species suggest that either the tracer velocities are considerably different due to sorption or size exclusion, or that phage followed very different flow paths and could reflect different entry points into the conduit system but similar exit points at major discharges.

An alternative explanation could be differential sorption of phage which could serve to retard the arrival of tracer peaks although at pH typical of Chalk groundwater $\Phi X174$ is thought to sorb more strongly rather than vice versa. Since $\Phi X174$ is of similar size to $MS2$ differences due to size exclusion can be considered to be negligible.

Based upon the data provided by the tracer testing and the review of existing data regarding the aquifer and the karst system conducted in chapters 3 and 4 it is now possible to define a new conceptual model for the function of the Hertfordshire Karst system and quantitatively parameterise the system in a manner that is consistent with the geology, hydrogeology and geomorphology. This in turn, can then provide new insights into the transport of bromate in the aquifer.

Chapter 6

A New Quantitative Conceptual Model of the Hertfordshire Chalk Karst

The catchment scale tracer tests have provided new information about the distribution and characteristics of karstic flow paths. In this Chapter, analysis of the quantitative tracer breakthrough curves has been undertaken using a number of one dimensional models.

6.1 Geometry and Distribution of Karst Flows

A summary of the established connections from the 20th century tracer tests (Harold, 1937) and those more recently, are presented in Figure 6.1.

The tracing suggests that there is a distributive karst flow system in Hertfordshire developed in a broadly north east direction between North Mymms and the Lee Valley. This system is characterised by rapid, low attenuation transport and probably follows the pattern of surface karst and swallow holes between the Palaeocene Feather Edge and the River Lee. The occurrence of the swallow hole tracer at a number of wells in the Lee Valley suggests either that development of karst is widespread throughout the aquifer in this area, or that long term operation and aquifer development around the abstraction wells has encouraged the convergence of rapid flow paths to these discharge points.

Rapid flow paths also appear to extend further west beyond the zone of main karst development into the Vale of St Albans. Flow velocities from tracing show a higher degree of variation in this area compared to those from Swallow Hole injections, and transport is more attenuated, suggesting that there could be multiple rapid flow paths perhaps reflecting a range of dissolution-enhanced fracture sizes, possibly as a result of infilling, weathering and/or erosion of karst features with increasing distance from the Palaeocene feather edge. Furthermore, the consistency of connections for all three tracers to major springs at Arkley Hole and Lynchmill Spring might suggest that these flow paths follow karstic routes that were probably established prior to the more recent development of abstraction wells. Recovery of all three tracer species at Essendon PWS suggest that this abstraction borehole it might be directly connected to the karst conduit system either by its construction of through development of the aquifer in the vicinity of the well.

Tracing from Water End and the Catherine Bourne has provided evidence that connectivity to the karstic features of the Mymmshall Brook system extends along the entire Palaeocene feather edge between the Lee Valley as far south as Turnford PWS and at least as far west as south east Hatfield and also possibly to north western Hatfield. The progression of tracer arrivals suggests that flows could be coincident with the pattern of surface karst and swallow holes between the feather edge of the Palaeocene outcrop and the River Lee and is consistent with karst flow paths intersecting the apparent bromate "plume" in the Hatfield area. This appears to be more geologically consistent than earlier conceptual models (e.g. Buckle, 2002) which have suggested a fan like series of major flow routes between Water End and the Lee Valley.

There is some evidence to suggest that karstic rapid flows extend further west beyond the zone of main karst development away from the Palaeocene feather edge into the Vale of St Albans and may bypass the catchment of Hatfield PWS. Flow velocities here are lower and transport is more attenuated, suggesting that karst is less continuous in the Vale of St Albans and is possibly restricted by infilling, weathering and/or erosion beyond the Palaeocene feather edge

The implication of possible by-pass of Hatfield PWS by the Vale of St Albans karst routes, and by bromate transport is that the influence of Hatfield PWS does not extend far north. Bromate may be entering the karst flow system to the north and east of the Comet Way borehole; hence scavenge pumping at Hatfield PWS only has a partial influence on down gradient concentrations and so cannot to provide completely effective protection to downgradient wells. This is supported by the relatively low recovery of the Water End tracer at Hatfield PWS.

The lack of tracer appearance at Chadwell Spring in the present tracer tests suggests, that flow to this spring has been affected by recent changes in abstraction patterns, supporting the evidence from water chemistry (Hydrotechnica, 1988; Assem, 2005) that it now derives water from further north, outside the catchment area of the tracer. This is consistent with bromate concentrations being typically lower at Chadwell spring than other locations to the south.

Apparent changes in the catchment of Chadwell Spring, in addition to the faster tracer arrival at Hoddesdon and Lynchmill spring, in this and the tracer tests of (Harold, 1937) suggest that the Northern Loop of the Palaeocene Feather Edge and River Lee is bypassed by subsurface karst which provides a faster to the central Lee

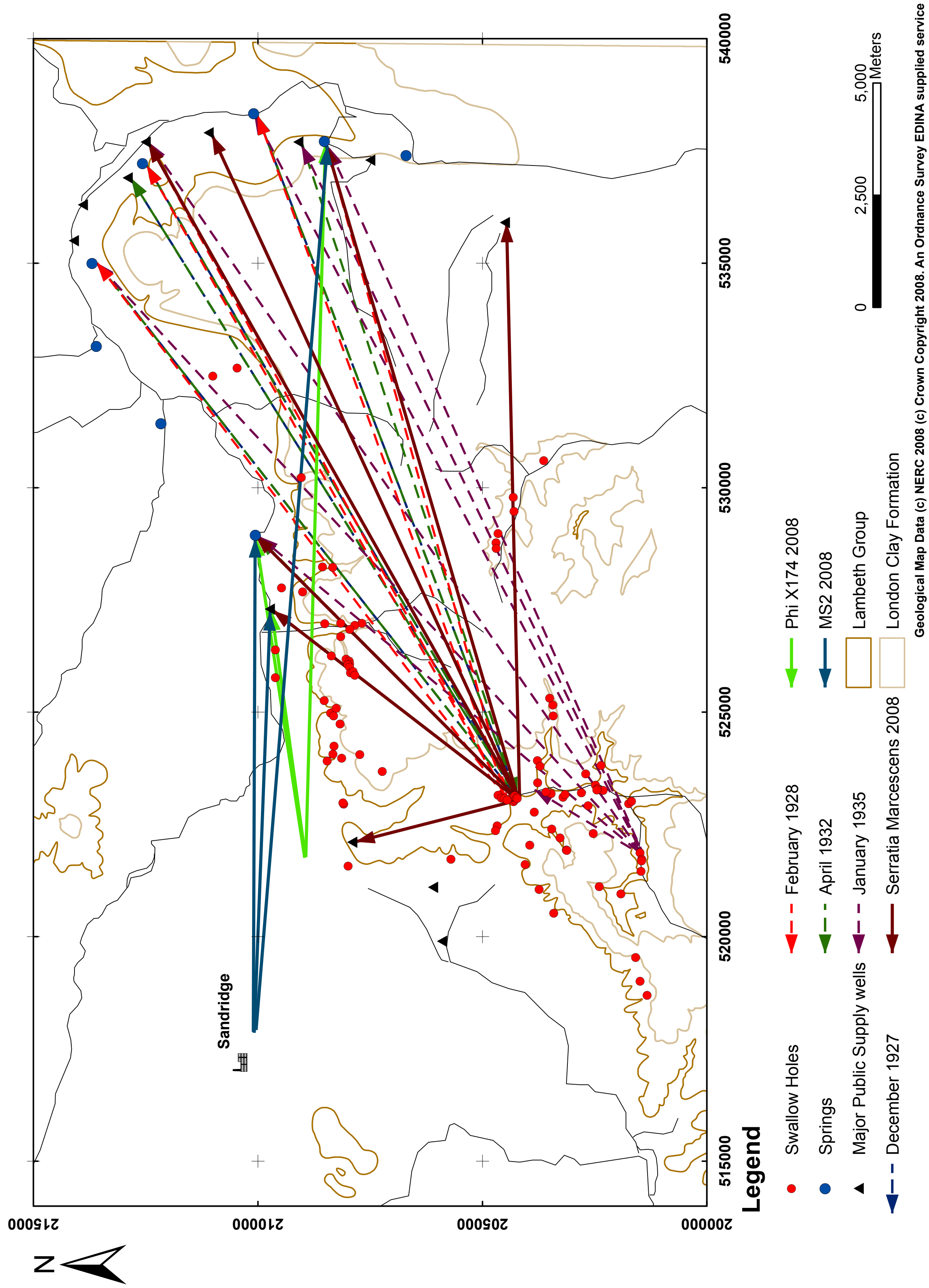


Figure 6.1: Established tracer connections in the bromate affected area of Hertfordshire

Valley. Consistency in the form of breakthrough at Essendon PWS and Arkley hole suggest this occurs east of Arkley Hole Spring.

The consistency of connections between all three tracer injection locations and the major springs at Arkley Hole and Lynchmill Spring suggest that these springs terminate karstic flow routes established prior to the more recent development of abstraction wells. Recovery of all three tracer species at Essendon PWS as well as similarities in bromate concentrations and turbidity at Essendon PWS and Arkley Hole Springs implies that Essendon PWS is also probably directly connected to the karst system.

The implication therefore is that a major flow pathway exists between the Essendon area and the Southern Lee Valley, aligned approximately east-west and terminating at Lynchmill Spring with distributary connections, influenced by abstraction, to Amwell Marsh, the Rye House/Rye Common Area, Hoddesdon and further south to Turnford and may explain why bromate concentrations are higher in the southern part of the Lee Valley. Such a connection might also explain the strong statistical correlation with concentrations at Essendon PWS with Hoddesdon PWS and Turnford PWS identified by Robinson and Buckle (2004). This flow pathway is aligned approximately sub-parallel to the Hoddesdon Syncline, suggesting a possible structural influence.

6.1.1 Location of Conduits

Since the general geometry of karst flows between the Vale of St Albans and the River Lee catchment has been established by tracing, the distribution of surface karst and aquifer structural features can be used to derive the likely locations of major karst conduit flow routes in Hertfordshire.

The distribution of swallow holes and dolines in Hertfordshire is shown in figure 4.8, these have been replotted in Figure 6.3 with the approximate elevation of the swallow holes and the approximate surface water catchments drained by the features estimated from OS topographic mapping following the method of Worthington (2003). The likely location of faults in the Hatfield area is also shown.

Connecting the swallow holes within each catchment by declining elevation, and guided by the tracer connections enables the positions of conduits to be estimated. The distribution of conduits using this method is presented in Figure 6.2. The estimated arrangement of conduits is consistent with the known distribution of surface karst, aquifer structure, and the connection of flows from the tracer testing. However, it is recognised that this is likely to be a simplification of the true conduit system. A fuller representation could be obtained from further tracing of other major swallow hole clusters, for example those at Gobions Wood and Hatfield Park.

Swallow Holes in the Mymmshall Brook catchment appear to drain a major conduit route flowing north, possibly exploiting faults in the Hatfield area. The

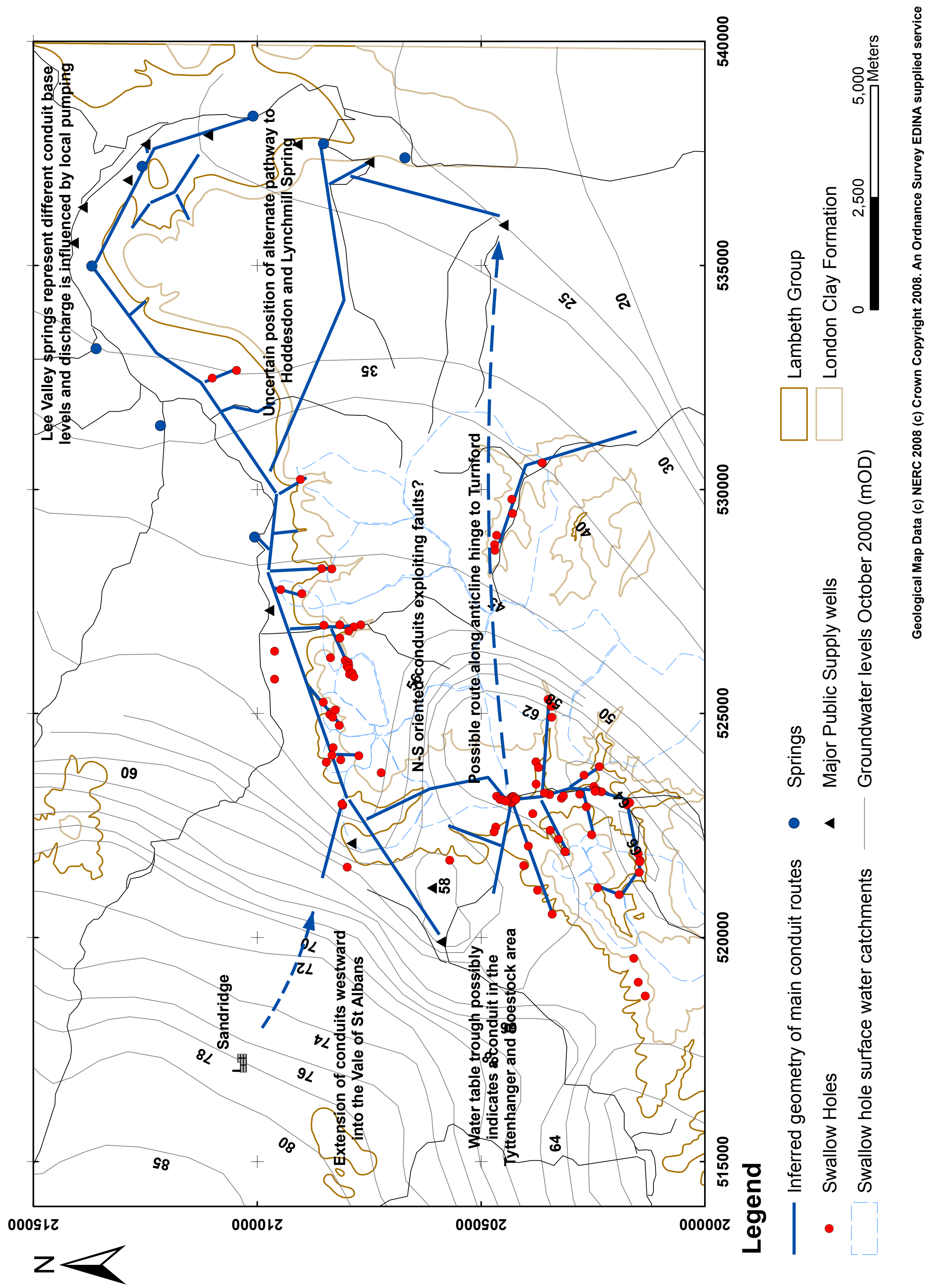


Figure 6.2: Estimated arrangement of main conduits/karst flow routes based on surface karst and drainage distribution, tracer test connections and structural features

conduit system then appears to turn eastward towards the Lee Valley, reflecting the arrangement of the surface karst developed along the Chalk-Palaeocene boundary. This also possibly reflects flow routes sub-parallel to the River Lea, and older routes following the alignment of the Proto-Thames. The Arkley Hole and Woolmer's Park springs might have originated as the river eroded into a zone of active conduits in this area; the sites now provide an outlet or inlet to the system depending upon the relative groundwater and river water levels. This major karst route probably receives contributory flows from swallow holes at the necks of smaller surface water catchments developed on the Palaeocene Escarpment.

Faults appear to be important in the development these tributary routes, either by establishing erosion and dissolution of N-S aligned valleys into the Palaeocene escarpment, and/or by focusing conduit development or rapid flows along the axes of fault features.

East of Arkley Hole there appears to a major karst flow diversion. Earlier timing of tracer arrivals at the Hoddesdon area and Lynchmill Spring than locations further north, for example Chadwell Spring, and Emma's Well suggest there are at least two major flow routes, one extending northwards to Chadwell Spring and the Amwell Marsh area, the other more directly eastward towards Lynchmill Spring, Hoddesdon and possibly to locations further south such as Turnford PWS. The precise location of this divergence is unknown since there is reduced occurrence of surface karst due to extensive outcrop of relatively Lowestoft Till and London Clay; the Chalk and Reading Formation rarely outcrop east of Woolmers park except in the base of the Lee Valley. Diversion could therefore occur anywhere east of Arkley Hole Spring. The most likely cause is a structural feature in the Chalk, most likely to be the axis of the Hoddesdon Syncline. There suggestion of a possible fault in a straight east-west aligned stream valley in the London Clay between Cowheath Wood and Hoddesdon, which is also aligned with the location of Lynchmill Spring.

The overall system appears to consist of recharge area comprising a convergent branchwork of conduits centered around the Mymmshall Brook Catchment and the North Mymms water table mound. This region drains along a solution-enhanced pathway developed adjacent to the Chalk-Palaeocene boundary to a distributary system developed to springs in the Lee valley. The karst connection to a number of public supply abstraction wells is possibly deliberate since a number are located close to known springs (i.e. Broadmeads PWS and Chadwell Spring, Amwell Marsh PWS and Emma's Well, Rye Common and Rye House Spring, and Hoddesdon/Middlefield Road and Lynchmill Spring) and the majority have extensive adit systems. It is also possible that the long history of abstraction, and development of porosity around the wells (for example by acidification) might have developed a connection with major natural flow systems.

Having established the spatial arrangement of the conduits it is possible to obtain

Table 6.1: Relationship between straight line distance from Water End and the two dimensional conduit distance based upon the estimated conduit arrangement

Location	Straight Line Distance x_l (m)	Estimate of 2D Conduit Path length x_c (m)	Sinuosity
Hatfield PWS	3207	4385	1.37
Essendon PWS	6800	9062	1.33
Arkley Hole Spring	8096	10582	1.31
Chadwell Spring	15081	18003	1.19
Emma's Well Spring	16340	20256	1.24
Amwell Marsh PWS	16585	20542	1.24
Rye Common PWS	16361	22443	1.37
Turnford PWS	13067	22914	1.75
Lynchmill Spring	15279	19884	1.30

an estimate of the sinuosity of the conduit flow paths compared with that of a straight line flow path by comparing the relative lengths of the two. Sinuosity is then given by x_l/x_c where x_l is the straight line distance and x_c is the conduit length. These have been estimated based upon the conduit arrangement in Figure 6.2 are presented in Table 6.1.

The sinuosities of the conduit system fall in the range 1.24 and 1.37, with most locations having a sinuosity approximately 1.3, consistent with other karst aquifers which show the sinuosity of conduits between 1 and 1.5 (Field and Nash, 1997). However, the tabulated values are underestimates of sinuosity since they do not incorporate the additional sinuosity imposed by changes in vertical elevation of the conduits. This can be estimated for the Arkley Hole, Chadwell Spring, Emma's Well and Lynchmill springs at least where the base levels of the discharge points are known and assuming the conduit entry and exit point is at local ground elevation. The vertical extent of the conduit system and possible constraining factors are discussed in Section 6.1.2.

6.1.1.1 Turnford PWS and the Conduit System

Establishing the conduit geometry in the vicinity of Turnford PWS is more uncertain than for other locations since there is relatively little surface karst known south of Lynchmill Spring, reflecting the presence of the London Clay and widespread alluvial deposits. That karstic development has occurred in the vicinity of Turnford PWS is indicated by the recovery of tracer with rapid flow velocities from Water End and karst is also hinted at by borehole construction drawings.

In developing the estimated conduit arrangement it was assumed that karst flows reaching Lynchmill Spring intersected southward-orientated flows developed along the Palaeocene boundary and perhaps via conduits developed below and parallel with the course of the River Lee, consistent with the regional hydraulic gradient dipping southward into the London Basin.

However, the Turnford route as arranged shows a difference in sinuosity, Turnford PWS also shows a slightly different form of tracer breakthrough, with a longer apparent tail at high concentrations followed by a relatively sharp return to background concentrations. To some extent the relatively long sampling intervals at Turnford PWS might explain this, the high concentration apparent tailing perhaps being caused by a secondary peak. An alternative, when considered in combination with the anomalous sinuosity, is that it could be indicative of a different flow path operating to Turnford.

One possibility, consistent with the observed geology, would be a karst route almost of exact east-west alignment from Water End along the axis of the Cuffley-Northaw Anticline which could incorporate tributary flows from the Great Wood and Cuffley Brook swallow holes. Tracing of flows from these swallow holes would help to establish if this is a genuine flow path.

6.1.2 Vertical Extent of the Conduit System

Establishing the vertical extent of karst carries additional uncertainty because of the paucity of data relating to the vertical stratification of the aquifer flows, the absence of deep exposures of the Chalk and inadequate borehole log descriptions. However, the elevation of known karst features and other related features provide constraints on the dimensions of the system.

Swallow holes and other epikarst development provide the uppermost constraint on the elevation and act as the recharge input to the karst system. The elevations of main swallow hole catchments are indicated on Figure 6.3. The elevation of swallow holes closely mirrors that of the Palaeocene-Chalk boundary, the highest set being those of the Potwells and the upper part of the Catherine Bourne at approximately 100mOD. in the core of the Cuffley-Northaw Anticline. The general elevation drops into the valley of the Mymmshall brook between 75 and 80m. Most swallow holes along the Palaeocene escarpment are within this range, although as the elevation of the Palaeocene-Chalk boundary drops eastward so do the swallow holes, the lowest set at Brickendonbury occur at approximately 50m. Considering groundwater elevations, this suggests a thickness of epikarst in the unsaturated zone of between 10 and 20m which is reasonably consistent across the aquifer, except beneath the highest swallow holes above the North Mymms water table mound where it reaches more than 30m in thickness.

Springs may be taken as indicative of the base level of major conduit development (White, 1993);, the elevation of known connected karst springs in the area is presented in Table 6.2. The elevations of the springs decrease eastward of Arkley hole and southwards along the Lee Valley, perhaps reflecting the drop ground surface in elevation due to the dip on the Chalk. It is possible that the springs represent different base levels at which conduits have been exposed in the valley of the River Lee with different springs operate under different groundwater conditions. However,

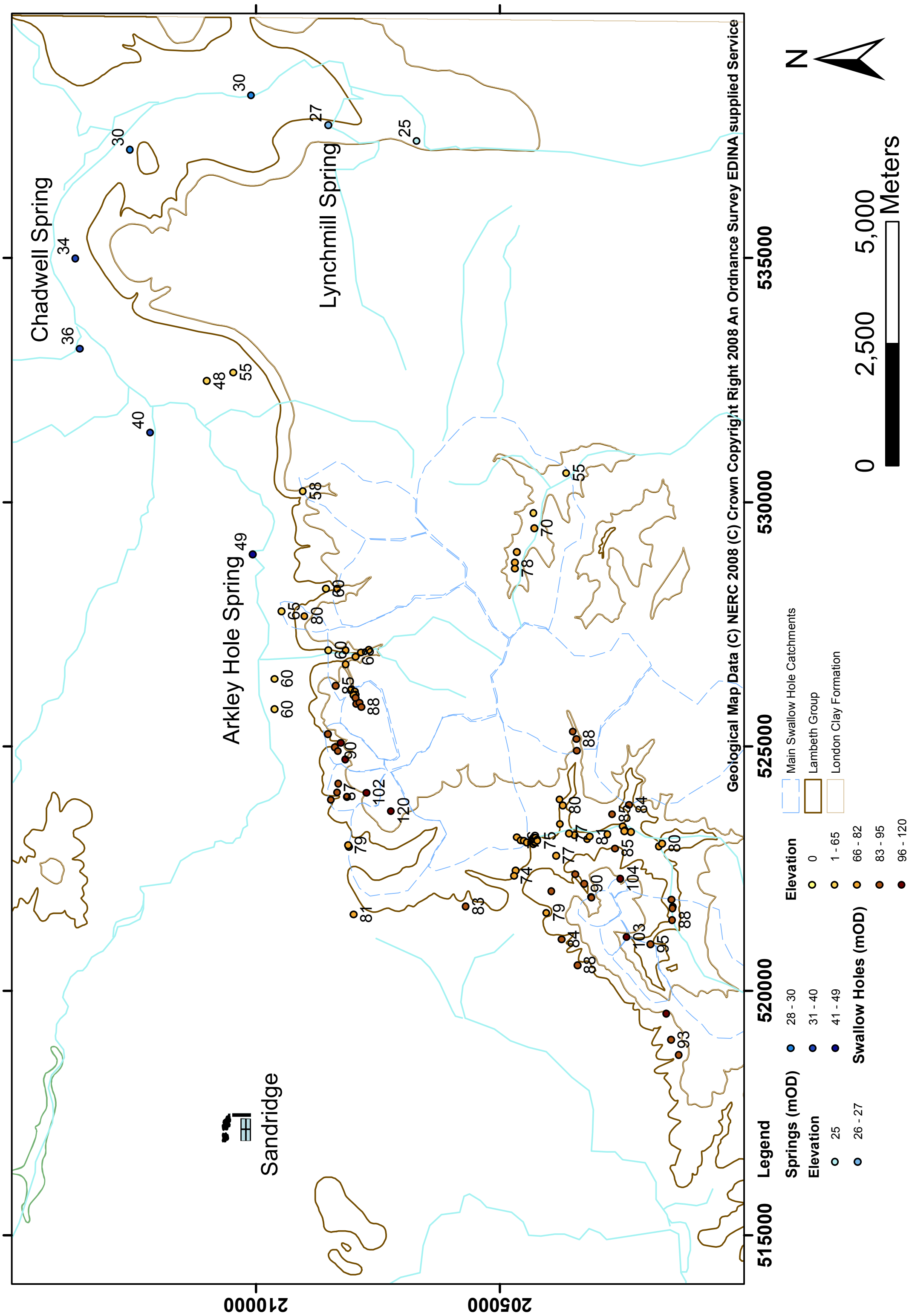


Figure 6.3: Elevation of main swallow hole catchments between the Mymmshall Brook Catchment and the Lee Valley

Table 6.2: Elevation of major karst springs in Hertfordshire. * The approximate elevation of Rye House Spring is given at its assumed location adjacent to Rye House.

Name	Easting	Northing	Elevation (mOD)
Arkley Hole Spring	528287	210050	49
Chadwell Spring	534972	213695	34
Emma's Well	537250	212620	30
Rye House Spring*	538536	209930	27
Lynchmill Spring	537743	208555	25

Table 6.3: Estimates of the mean depth of conduit flow in the Hertfordshire Karst system using the empirical relationships determined by Worthington (2001, 2005). Where D is the mean conduit depth in metres below the water table, L is the flow path length in metres, taken to be 25367m assuming the flow path follows the conduit arrangement outlined above from the Highest swallow holes on the Catherine Bourne to Lynchmill Spring (the Lowest spring), θ is the sine of the dip taken to be at 2^o, E is the elevation difference in metres between the lowest spring and the highest swallow hole (75.5m).

No.	Relationship	Correlation Coefficient	Mean depth of conduit flow (m)
1	$D = 0.053L^{0.77}$	0.64	130.5
2	$D = 120\theta^{0.56}$	0.5	18.3
3	$D = 0.60E^{0.74}$	0.68	14.7
4	$D = 0.061L^{0.91}\theta^{0.72}$	0.9	55.5
5	$D = 0.016L^{0.54}E^{0.56}$	0.8	0.58
6	$D = 1.6E^{0.64}\theta^{0.72}$	0.7	2.3
7	$D = 0.047L^{0.85}\theta^{0.64}E^{0.11}$	0.9	48.9
8	$D = 0.18(L\theta)^0.81$	0.79	43.9

since the elevation of all springs is below the elevation of groundwater in the recharge zone of the Mymmshall Brook a relatively constant discharge could reasonably be expected as long as there is flow into the feeding swallow holes. Nevertheless, spring discharge may still be affected by nearby abstraction.

Comparing the relative elevations of the highest water table beneath swallow holes ($\approx$ 70mOD) in the North Mymms recharge mound and the lowest spring level ($\approx$ 27mOD) gives a total karst thickness of 43m. Worthington (2001, 2005) has derived a number of empirical relationships to determine the mean depth of conduit flow for various karst catchments. These have been used to give an estimate of the likely mean depth of flow for the Hertfordshire Chalk (Table 6.3).

The depth estimates using these empirical relationships are highly variable, ranging from just below the water table to approximately 50m below the water table, the best correlated relationships to observed conduit depths suggest depths of 49-56m below the water table, close to the estimate of total karstic thickness in Hertfordshire based on the relative elevation of stream sinks and springs. Ford (2002); Ford and Williams (2007) have argued against these relationships and propose that the actual maximum depth of conduit flow is constrained by the depth of availability of open fracture. In the Chalk the base of the effective aquifer is typically taken as being 60m below the water table, in close agreement with the best correlated estimates of 49-56m.

Subsurface observations of conduit depths in the Chalk, for example using geo-

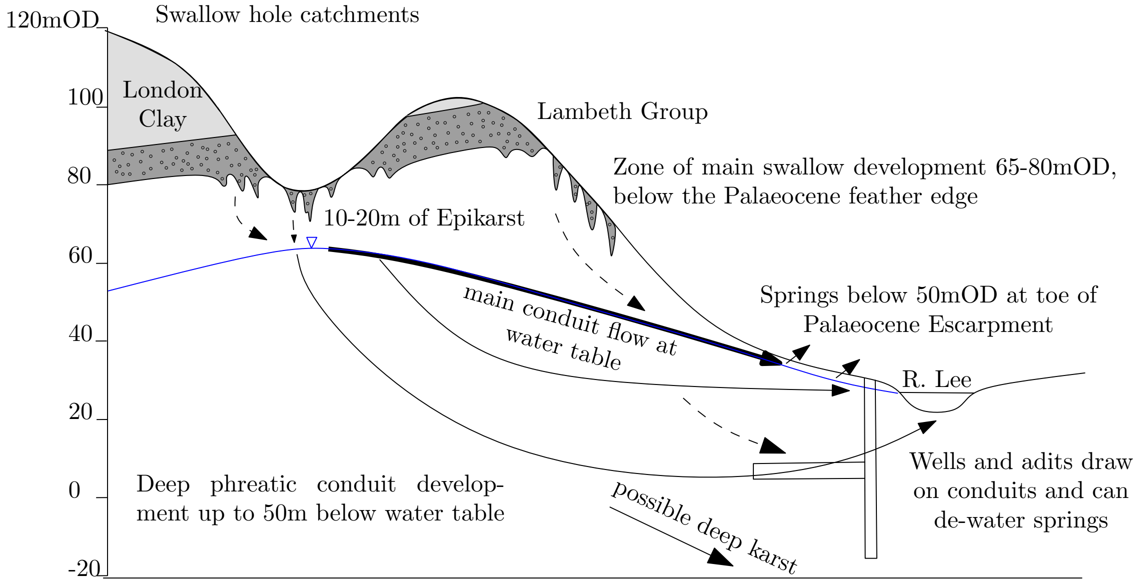


Figure 6.4: Schematic cross section summarising the vertical geometry of the karst conduit development. The vertical scale has been greatly exaggerated

physical optical methods (e.g. Banks et al., 1995; MacDonald et al., 1998), most commonly place them at elevations at or close to the level of the present (and/or past) water table(s) which would appear to agree closely with the elevations of spring discharges, however Maurice (2008) could not establish a clear relationship between conduit depth and occurrence, although fracturing and stratigraphic features were important.

The most likely situation in Hertfordshire is that the major conduits are developed at or just below the zone of water table fluctuation. Relatively stable groundwater elevations east of Hatfield reinforce this possibility since the water table may be controlled by the high transmissivity of such features. However, there remains the potential for conduits to have developed throughout the whole depth of the effective aquifer, and the limited evidence from Turnford PWS of sand-filled fractures > 100mbgl (≈ -70mOD) suggest that this might have occurred, giving a maximum karst thickness, including the epikarst zone of 170m i.e. covering the whole of the Seaford, Lewes Nodular, New Pit and Holywell Nodular Chalk formations. The vertical arrangement of conduits is summarised in Figure 6.4

6.2 Transport Parameters of the Karst System

Having established constraints on the spatial extent of the conduit system, the tracer test data provide new information regarding the transport properties of the flow system. Flow velocities have already been discussed in Chapter 5 and for the main karst system are typically in the range 2-4km/day, consistent with karst flows seen elsewhere in the UK Chalk and for other karstic aquifers (Worthington, 2001). The determination of quantitative tracer breakthrough curves (TBC) go beyond what was achieved in the 20th century tracing tests and allow interrogation of the data to determine transport parameters and, in the context of the conceptual model outlined additional parameters regarding conduit geometry.

Hydrodynamic dispersion of solutes arises through differential variations in flow velocities, the tortuosity of pathways and through diffusion. The contribution of diffusion for most cases is relatively small, as it is a slow process compared to that of the groundwater flow velocity. Despite this, in double porosity aquifers such as the Chalk, additional dispersion can occur due to the diffusive exchange of solutes between the mobile groundwater in fractures and/or conduits and the immobile matrix pore water. Dispersion, along with flow velocity is therefore one of the key parameters in characterising solute transport.

The quantitative tracer breakthrough curves have been analysed using three different analytical packages which in combination reveal different characteristics of the transport processes.

Table 6.4: Description and parameters determined by the analytical models used for quantitative tracer breakthrough curve analysis

		Parameters Determined				
Model	Description	Travel time Statistics	Velocity Statistics	Dispersivity	Peclet Number	Mass Transfer Coefficient
Qtracer2	Program for analysis of quantitative tracer breakthrough curves based upon a method of moments analysis. Solute transport is not simulated and the tracer is always assumed to be conservative USEPA (2002)	✓	✓	✓	✓	×
CXTFIT	Analytical model used to simulate one dimensional transport by the advection dispersion equation. Options for incorporation of sorption, inactivation and two region transport are available (Toride et al., 1995)	×	✓	✓	×	✓
DP-1D	One dimensional analytical transport model for simulating double porosity transport incorporating a full model of diffusion to immobile matrix porewater (Barker, 2005)	✓	×	✓	×	✓

The tracer test data were initially analysed using the Qtracer2 software (USEPA, 2002). Qtracer2 which estimates statistics describing tracer travel time, groundwater velocity and dispersivity based upon a methods of moments analysis of the tracer breakthrough curve. Transport distances were corrected by sinuosity factors (Table 6.1) and transport was assumed within a subsurface channel network. The Qtracer2 analysis assumes that the peak observed tracer concentration is equal to the actual peak concentration and interpolates the tracer breakthrough curve from the available data points using a "piecewise cubic Hermite" function (USEPA, 2002). Dispersivity is estimated by fitting a straight line to a plot Chatwin parameter against early time data. The estimated parameters for the tracer breakthroughs are presented in Table 6.5.

Table 6.5: Derived parameters for each tracer breakthrough using the Qtracer2 software package. t_{break} is the breakthrough time, t_{peak} is the peak travel time, $\bar{t}$ is the mean travel time and σ_t is the standard deviation of travel times.

Location	Travel Times (hours)				Velocity (m/s)			Dispersivity	Peclet Number
	t_{break}	t_{peak}	$\bar{t}$	σ_t	v_{max}	$\bar{v}$	σ_v	α_L (m)	Pe
Water End Breakthroughs									
Hatfield PWS	22.26	43.82	44.60	13.56	0.05482	0.02737	0.00818	203.18	21.62
Essendon PWS	42.55	67.37	82.12	55.34	0.05904	0.03059	0.00941	111.13	81.38
Arkley Hole Spring	53.14	70.06	74.53	24.76	0.05545	0.03953	0.00640	24.04	441.14
Amwell Marsh PWS	94.89	165.70	165.08	25.63	0.06020	0.03461	0.00590	247.83	82.98
Rye Common PWS	96.85	213.52	243.93	52.94	0.06429	0.02552	0.00653	527.79	42.47
Lynchmill Spring	92.26	105.06	120.95	46.90	0.05980	0.04562	0.00857	47.90	414.66
Turnford PWS	94.37	167.32	205.21	86.16	0.05769	0.02653	0.00944	294.51	66.55
$\Phi X174$ **Breakthroughs**									
Essendon PWS	148.96	191.94	190.71	11.85	0.01053	0.00822	0.00054	10.89	518.13
Arkley Hole Spring	193.38	216.48	229.64	22.85	0.01049	0.00883	0.00085	14.24	512.69
Lynchmill Spring	189.78	287.78	265.18	27.32	0.02335	0.01671	0.00181	84.67	188.43
$MS2$ **Breakthroughs**									
Essendon PWS	224.55	290.52	274.6	16.754	0.0119	0.00970	6.27×10^{-4}	17.84	537.23
Arkley Hole Spring	518.1	552.47	557.62	16.267	0.00602	0.00559	1.63×10^{-4}	1.13	9936.4
Lynchmill Spring	1223.6	1270.4	1288.1	29.164	0.00454	0.00432	9.80×10^{-5}	2.77	7227.5

The sampling frequency is therefore a source of error in these estimates, particularly so for TWUL locations which had a lower sampling interval. The springs which had the highest density of data also show the lowest apparent dispersivity since the peak and leading edge of the tracer breakthrough can be well constrained to within a few hours. Since observations for most locations, probably occur on the tail of the breakthrough this will cause the timing of peak breakthrough to be over estimated and as a result, mean travel times and velocities to be underestimated and dispersion to be overestimated.

Despite their overestimation the dispersivity values are in the range 24.4-527.5m for the Water End breakthroughs, 10.9-84.7m for the Comet Way breakthroughs and 1.1-17.8m for the Harefield house breakthroughs. Generally the estimates of dispersivity are relatively low when the scale of the flow path is considered as dispersivity is normally estimated based upon a function of the transport distance x_l usually taken to be $0.1x_l$. Over the transport distances seen in the tracer test of 10-20km, dispersion coefficients would be anticipated in the range 1000-2000m using the distance relationship or 23-28m using the empirical relationship of Xu and Eckstein (1995). The spring locations show the lowest apparent dispersivity, consistent with a more direct connection to the karst conduit system compared to the wells.

Dispersivity estimates for $\Phi X174$ are similar for Essendon PWS and Arkley Hole Spring which is consistent with other observations that these locations show similar behaviour. The estimated dispersion of $\Phi X174$ also is slightly lower than that of *Serratia Marcescens* bacteriophage. Lynchmill Spring shows much higher dispersion, possibly reflecting increased transport distance, however it is not outside the range of that estimated for the *Serratia Marcescens* tracer.

The apparent dispersivities are somewhat anomalous for MS2 suggesting both a low dispersion and an inverse relationship of dispersion with distance. This could be additional evidence to suggest that the apparent tracer recovery is not genuine, however it may also be consistent with an increased significance of channeling and conduit development with distance from injection. The nearer source breakthroughs might include a proportion of both diffuse fracture flow and conduit flow, but with increasing distance the conduit system dominates transport and the only breakthrough might represent a small pulse of early arrivals that have followed the fastest, least attenuating flow path, perhaps in a similar manner to observations by Taylor et al. (2004) for vertical penetration of bacteria in a sand aquifer .

The Peclet numbers provides an indication of the relative significance of advection and diffusion along the flow path. All connections indicate Peclet numbers ≥ 6, which is usually taken as the cut-off point where advection begins to dominate transport (Field and Nash, 1997) and are in keeping with low overall dispersion on the tracer breakthroughs.

Estimation of statistical parameters for time and velocities by the Qtracer2 allows determination of dimensionless standardised tracer breakthrough curves using the method of Mull et al. (1988) and direct comparison of the apparent tracer breakthrough curves at each location and are illustrated in Figures 6.5.

The standardized breakthrough curves show two distinct forms, that typified by Essendon PWS, Arkley Hole PWS and Lynchmill Spring of a sharp peak and pronounced tailing, and that shown by most of the PWS locations as well as the minor tracer breakthroughs from Comet Way and Harefield house which are more symmetrical in form with less tailing. However, the Qtracer2 software interpolates only between actual observations and for most PWS locations breakthroughs and as the standardized curves are based on incomplete data and sharp peak may have been missed.

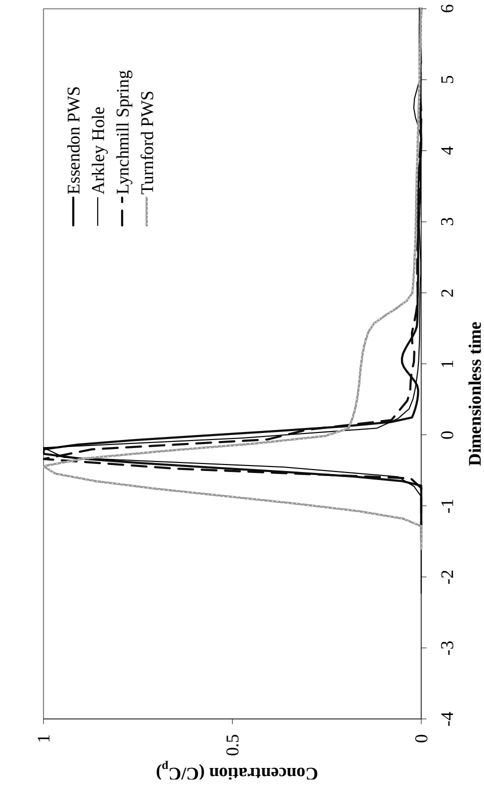
The similarity in Essendon PWS, Arkley Hole spring and Lynchmill spring breakthroughs is obvious, in part reflecting better data quality at these locations. Although the sampling frequency at Essendon PWS was the same as at Hatfield PWS, it appears that fortuitously a sample was taken at or close to peak breakthrough. However, the similarity and form of breakthrough might also reflect the strength of connection to the karst conduit system, by nature Arkley Hole and Lynchmill Spring have a direct connection and supporting turbidity data and the similarity to Arkley Hole suggests Essendon PWS may also be directly connected.

The similarity in form of all other breakthroughs may suggest a less direct connection to the conduit system, perhaps with a proportion of the transport occurring by more diffuse fracture-dominated flow feeding into conduits (as might be the case for Comet Way and Harefield House breakthroughs). Turnford PWS appears anomalous, showing a more dispersed peak and an extended tail of high tracer concentration which could be suggestive of an alternative transport route or mechanism, as was described in section 6.1.1.1.

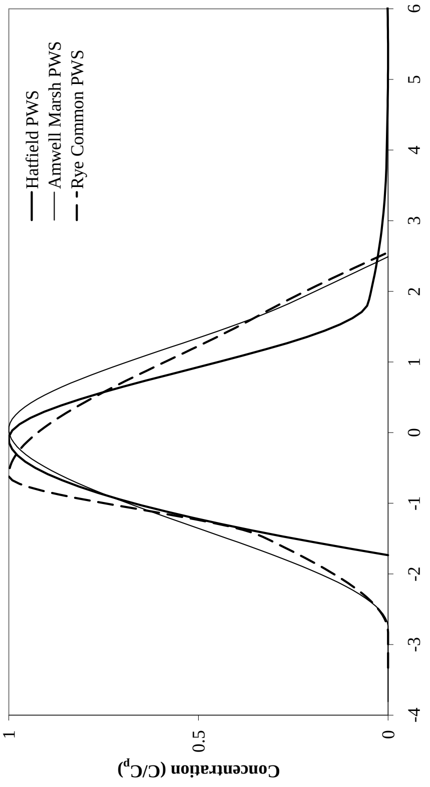
If tracing was repeated over a range of discharge conditions these standardised tracer breakthroughs could be used to derive “type curves” for the form of breakthrough, which in turn could be used to predict contaminant transport through the karst system. An example of this process is given by Mull et al. (1988).

6.2.1 Modelling of Tracer Breakthrough using the Advection Dispersion Equation

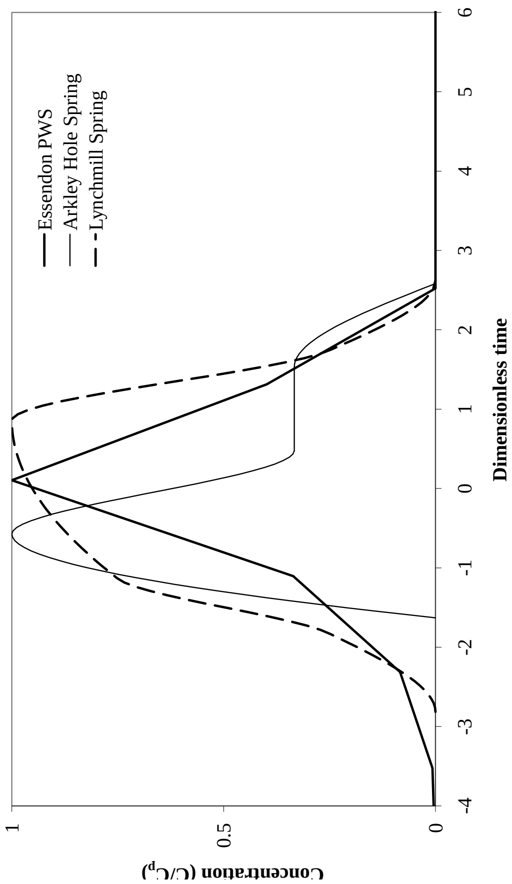
Qtracer2 is based upon statistical analysis of observations and does not include any physically based simulation of solute transport. Analysis of tracer breakthrough curves by the fitting of analytical solutions to the advection dispersion equation is a standard procedure for determining solute transport parameters (e.g. Ward et al., 1998; Atkinson et al., 2000; Carlier and Boulemia, 2002; Birk et al., 2005). Fitting of models to the bacteriophage breakthrough curves was undertaken using the CXTFIT Version 2.1 software package (Toride et al., 1995). CXTFIT incorporates inverse



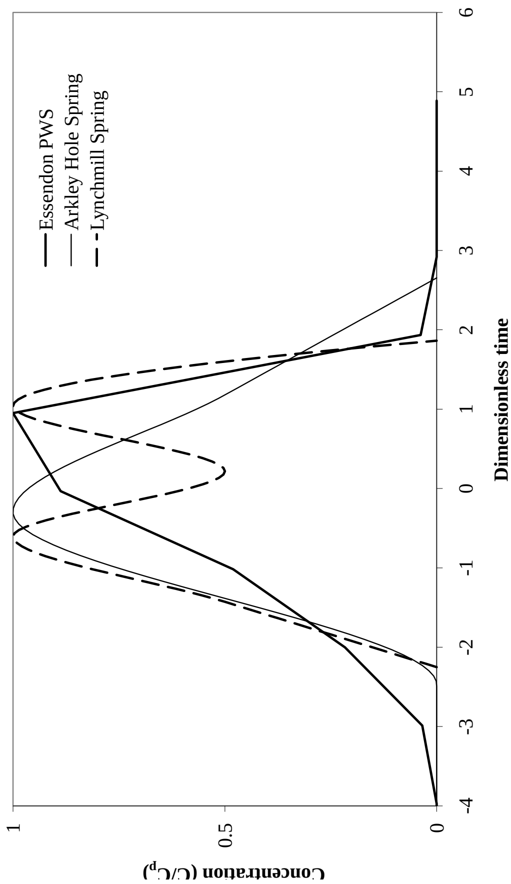
(a) Water End Type Curve 1



(b) Water End Type Curve 2



(c) $\Phi X174$ Tracer type curves



(d) $MS2$ Tracer type curves

Figure 6.5: Standardised breakthrough curves for the tracer breakthroughs; Essendon PWS, Arkley Hole Spring and Lynchmill Spring these locations which are probably the best constrained by observations show similar breakthrough forms. Turnford PWS also appears to be similar but is more intermediate between the main karst flows and those at PWS locations. All other locations, including breakthroughs from Harefield House and Comet way show similar overall form.

parameter estimation based upon fitting residuals using a least-squares approach.

Model fitting was undertaken using two conceptual models, in the first instance, mean flow velocity and dispersivity were estimated using a one dimensional conservative equilibrium solution to the Advection dispersion equation, these fitted parameters are presented in Table 6.6. At some locations, particularly the springs it is possible that tailing might be present and non-unique solutions to the advection dispersion model prohibits generating a meaningful fit to the data.

A two region (dual porosity) approximation has been applied to those locations which show tailing and which did not show a good fit to the equilibrium single region model, the fitted parameters for these locations are presented in Table 6.7.

An instantaneous (Dirac type) source was used to approximate the injection pulse. The real world case involves three dimensional advection and dispersion to a number of locations however the model can only incorporate one dimensional transport. To simplify analysis injection concentration at each location was estimated based upon the tracer recovery by resident concentration so that simulations and observations can be directly compared. This assumption approximates the actual transport conditions, but the approach has been used successfully to determine parameters in other tracer test analyses (e.g. Birk et al., 2005; Mathias et al., 2009).

The fitting of secondary peaks was excluded from the two region and diffusive double porosity approaches since these perturb the form of the tailing. It might in principal be possible to fit additional peaks through superposition of additional breakthrough curves, however the uncertainties of an input concentration for the secondary peaks, flow path information and the relatively sparse data will impose limitations on the accuracy of such an approach.

Sorption and inactivation were not incorporated in either modelling approach, since neither can be appropriately parameterised with any certainty under the conditions of the tracer test, i.e. for the Chalk aquifer, they have been excluded. Data presented in Section 5.2.1.1 suggest that sorption might be limited within the Chalk aquifer due to the low proportion of organic matter and iso-electric properties of the phage themselves. The close agreement of phage breakthrough times from Water End with those of conservative fluorescein dye of Harold (1937) suggest that there is little retardation of the initial phage breakthrough due to sorption, however the possibility of additional tailing due to non-linear or temporary sorption and/or inactivation. Phage inactivation may be an important but remain a poorly quantified factor, particularly for longer transport times of the MS2 and $\Phi X174$ phage, although (Skilton and Wheeler, 1989) demonstrated the long term survival of *Serratia Marcescens* in Chalk groundwater.

Table 6.6: Summary of fitted parameters to tracer Serratia Marcescens and $\Phi X174$ tracer breakthrough curves using the CXTFIT software package for an instantaneous pulse of tracer. The $MS2$ breakthroughs could not be fit using the software

Injection	Monitoring Location	Fitted Parameters			Dispersivity	Measures of Fit		
		Injection Mass (pfu)	Mean Velocity (m/s)	Dispersion Coefficient (m^2/hour)	(m)	Sum of Squares	Mean Square Error (pfu/ml)	Correlation Coefficient r^2
Water End	Hatfield PWS	16630	138.5	4169	30.1	1460	11.23	0.997
	Essendon PWS	12790	99.06	3210	32.4	316.8	45.26	0.999
	Arkley Hole Spring	30740	118.7	1372	11.56	14310	1022	0.999
	Amwell Marsh PWS	12750	92.74	7846	84.6	9.67×10^{-12}	1.93×10^{-12}	1.00
	Rye Common PWS	432.5	67.03	26250	386.3	0.0898	0.0299	0.987
	Turnford PWS	15550	78.89	10660	135.12	0.0299	0.897	0.987
	Lynchmill Spring	25030	143.3	5529	38.58	239600	6305	0.925
Comet Way	Essendon PWS	179.8	30.44	98.62	3.24	2.11^{-5}	$1.06 \times 10-5$ 0.999	
	Arkley Hole	98.23	39.21	347.3	8.86	0.984	0.246	0.867
	Lynchmill Spring	405.1	60.39	4254	70.44	0.169	0.0337	0.990

Table 6.7: Summary of fitted parameters for a two region advection dispersion model to *Serratia Marcescens* tracer breakthrough curves that show tailing using the CXTFIT software package (Toride et al., 1995) for a instantaneous tracer pulse. β is the proportion of mobile water involved in transport, the remainder is the proportion of immobile water involved. ω is the mass transfer coefficient.

Monitoring Location	Fitted Parameters					Dispersivity	Measures of Fit		
	Injection Mass (pfu)(m/s)	Mean Velocity (m^2/hour)	Dispersion Coefficient	β	ω (m)	α_x (m) Squares	Sum of Error (pfu/ml)	Mean Square Coefficient r^2	Correlation
Essendon PWS	16410	94.42	4151	0.94	3.58×10^{-6}	44.91	7.6	1.52	0.999
Arkley Hole Spring	32040	117.1	1236	0.98	1.24×10^{-5}	10.56	275.5	9.5	0.999
Lynchmill Spring	25380	139.4	1977	0.96	2.53×10^{-5}	14.18	1843	63.54	0.999
Amwell Marsh PWS	2671	101.2	429.6	0.92	3.04×10^{-5}	4.25	1.94×10^{-2}	6.45×10^{-5}	0.999
Turnford PWS	25370	69.1	284.7	0.92	1.62×10^{-5}	4.12	3.92	1.96	0.995

Table 6.8: Parameters derived from fitting the diffusive dual porosity model, DP-1D (Barker, 2005) to the tracer breakthrough curves from Water End injection which show tailing. The equivalent two region exchange coefficient, ω is calculated from $\omega = D_{im}\theta_{im}/(af_{s\to 1})^2$ given in (Barker, 2005) where a is the volume by area ratio of the hollow concentric cylinder ($a = \sqrt{t_c b D_{im}}$) and $f_{s\to 1}$ is a shape factor given in table 1 of (van Genuchten, 1985), since precise vales of $f_{s\to 1}$ for the determined values of a are not given, the closet provided value has been adopted.

Location	Characteristic Times			Mass Transfer Coefficient	Measures of Fit	
					Sum of Squares	Mean Square Error
	t_a	t_{cb}	t_{cf}	ω		
Essendon PWS	62.10	8.43×10^6	226004	1.15×10^{-8}	363366	24224
Arkley Hole Spring	67.47	1.05×10^7	29019	3.8×10^{-8}	11798	347
Lynchmill Spring	104.65	2.17×10^6	5998.49 2.49×10^{-7}	243083	5340	
Turnford PWS	146.00	7.49×10^5	2075.60 1.17×10^{-6}	183	30.53	

As an additional modelling approach, an analytical solution to the advection diffusion dispersion equation using the DP-1D code (Barker, 2005) was also employed. The DP-1D code explicitly codes a physical model of double porosity diffusion from mobile fracture water into immobile matrix porewater. As with the CXTFIT model, an instantaneous source was approximated by the total concentration recovery of tracer at each location. The DP-1D code also requires additional parameters compared to CXTFIT:

- An estimate of the mobile (fracture/conduit) and immobile (matrix) porosity. The mobile porosity was taken to be 0.02 for the estimated effective porosity of channel systems in the Chalk from Worthington (2003). The immobile porosity was taken from local field data for the Seaford Chalk formation in Robinson and Buckle (2004).

- Specific discharge was adjusted so that in combination with the effective porosity of the conduits the transport velocity in the mobile phase was equal to the velocity derived from the CXTFIT model.

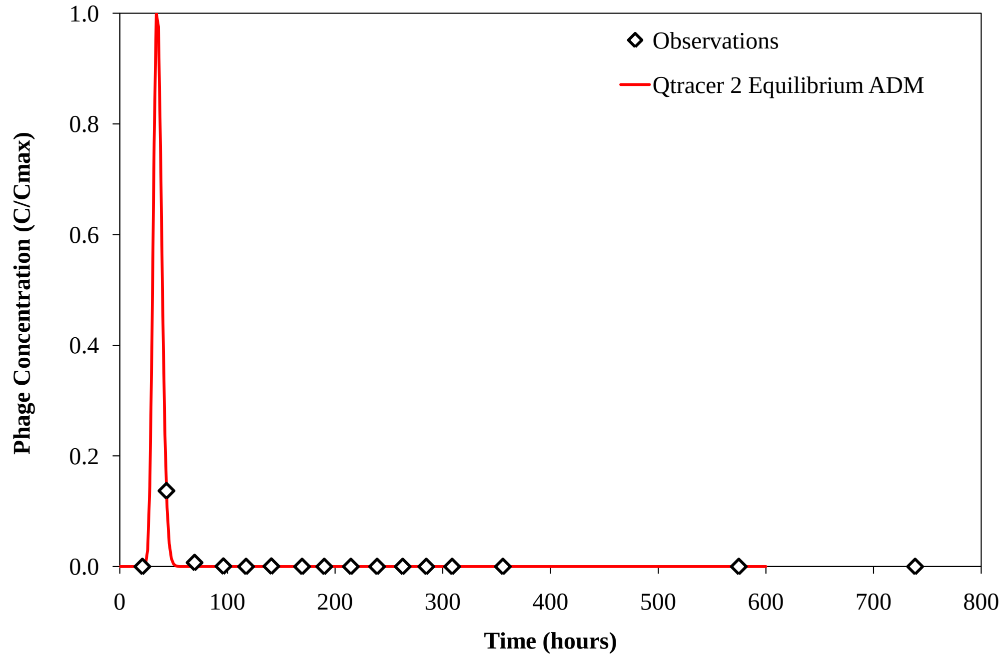
- A diffusion coefficient for bacteriophage of $7.06 \times 10^{-6}\text{m}^2/\text{hour}$ was derived from (Bayer and DeBlois, 1974).

- Transport distance was taken to be the apparent straight line distance.

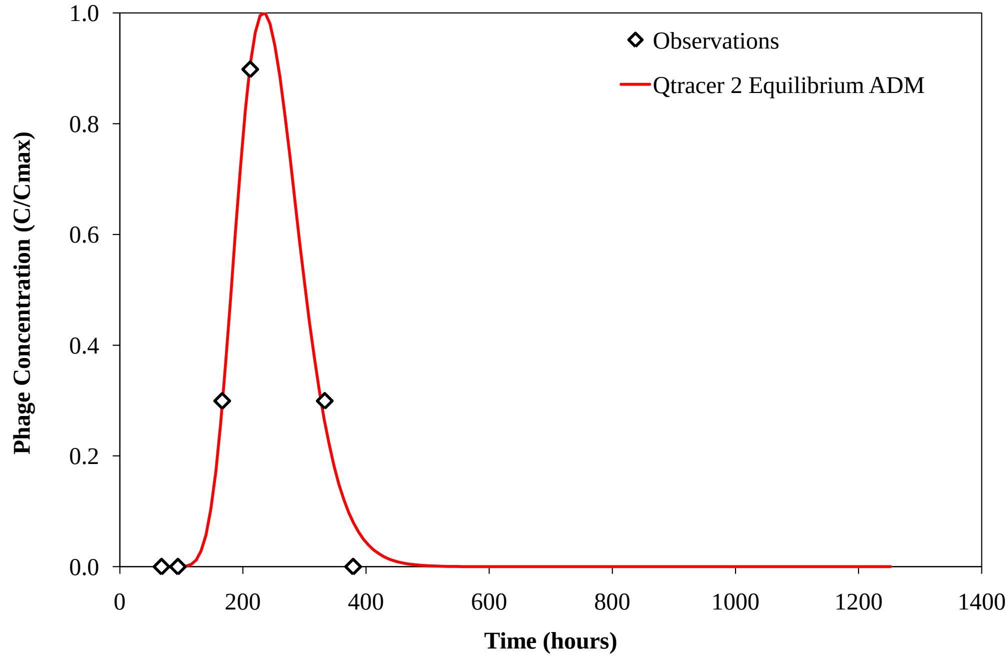
- A concentric cylinder shape factor was adopted as this most closely represents a karst conduit.

Those locations which show tailing of tracer concentrations have been fitted with both a two region CXTFIT and a dual porosity DP-1D curve and are shown in figures 6.8 and 6.9. Locations which can be reasonably well approximated by a simple advection and dispersion model are presented in figures 6.6 and 6.7, the latter also illustrates the problem of fitting the models to non-continuous data. A number of parameter combinations can be modelled with similar visual and statistical fit. The principal uncertainty being the timing of the initial breakthrough as a function of the transport velocity. Changes in velocity can cause the data to plot either on the tail of a peak (the most likely scenario) or on both the rising and falling edge and introduces uncertainty in estimated velocity and as a result similar variations in related parameters such as dispersivity.

The DP-1D curves were fit to the observed data by adjusting two parameters; the volume to area ratio b, and the ratio of the inner and outer radius of the concentric cylinders ρ, using a least square residual method. A number of combinations of b and ρ produce comparable fits and thus the solutions are also non unique. However, all fits follow the same general form to give $t_a < t_{cf} << t_{cb}$. Diffusion is therefore relatively insignificant in terms of the conduit transport although does play some role in extending the tracer tail at low concentrations.

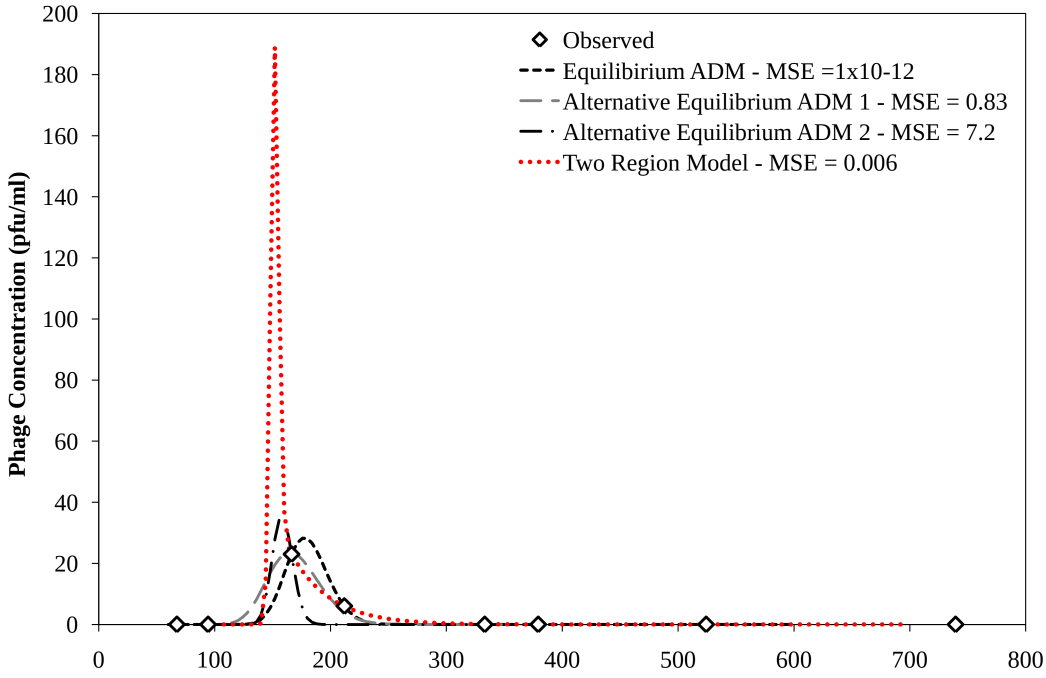


(a) Hatfield PWS

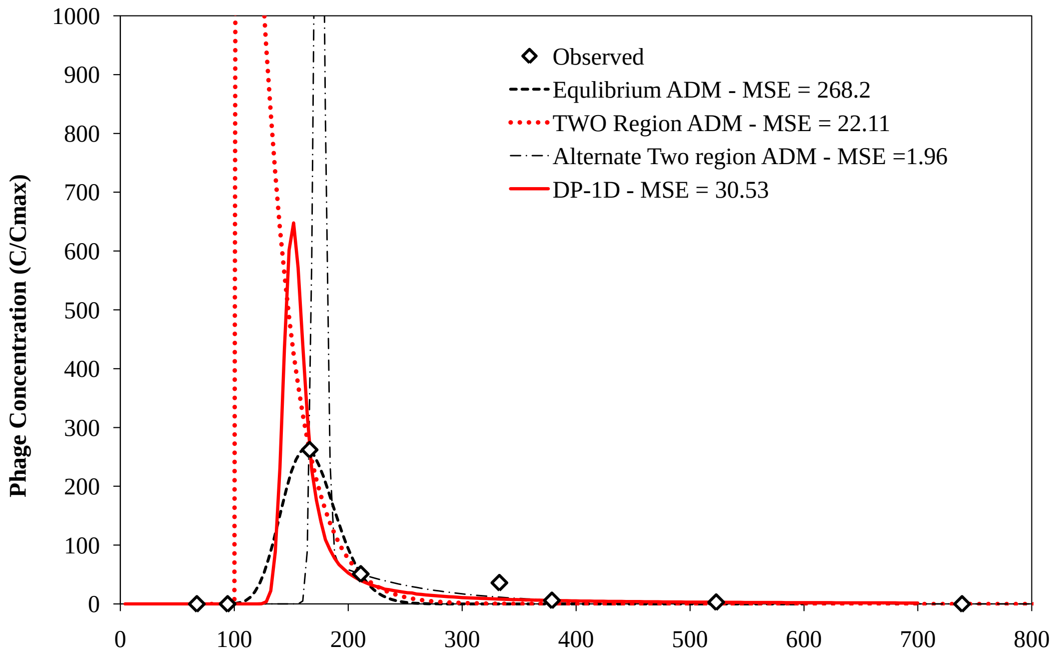


(b) Rye Common PWS

Figure 6.6: Fit of the Advection Dispersion Model (ADM) CXTFIT to observed tracer breakthroughs at Hatfield PWS and Rye Common PWS. Slight tailing of the breakthrough curve does occur at both locations, however the low concentrations of tracer in the tail mean that the statistical fit is not improved through the use of more complex models

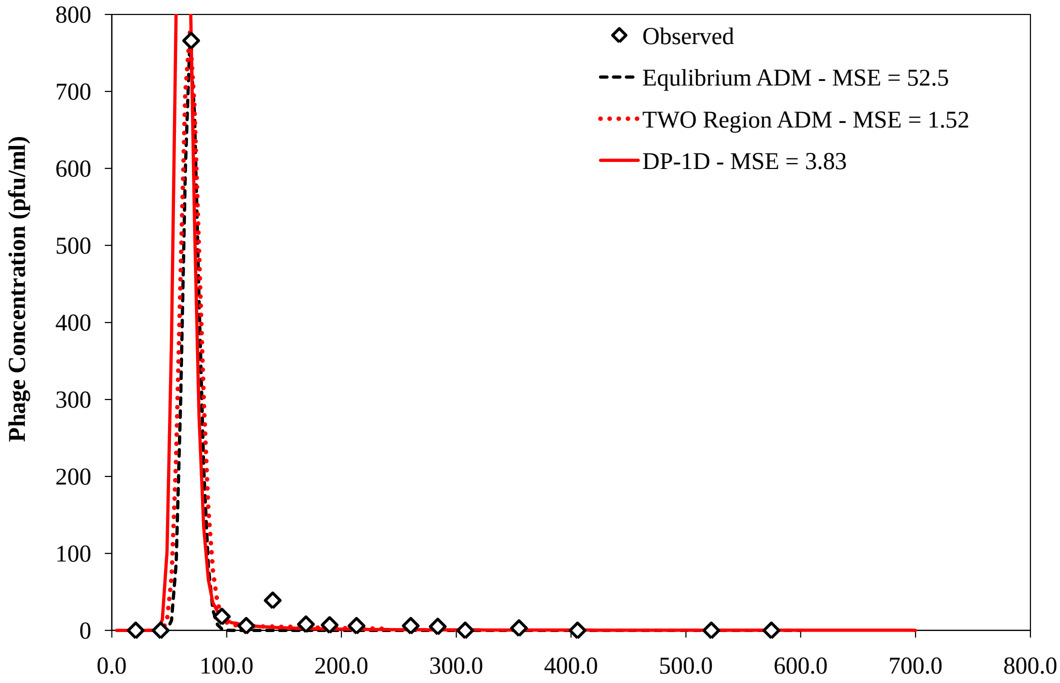


(a) Amwell Marsh PWS

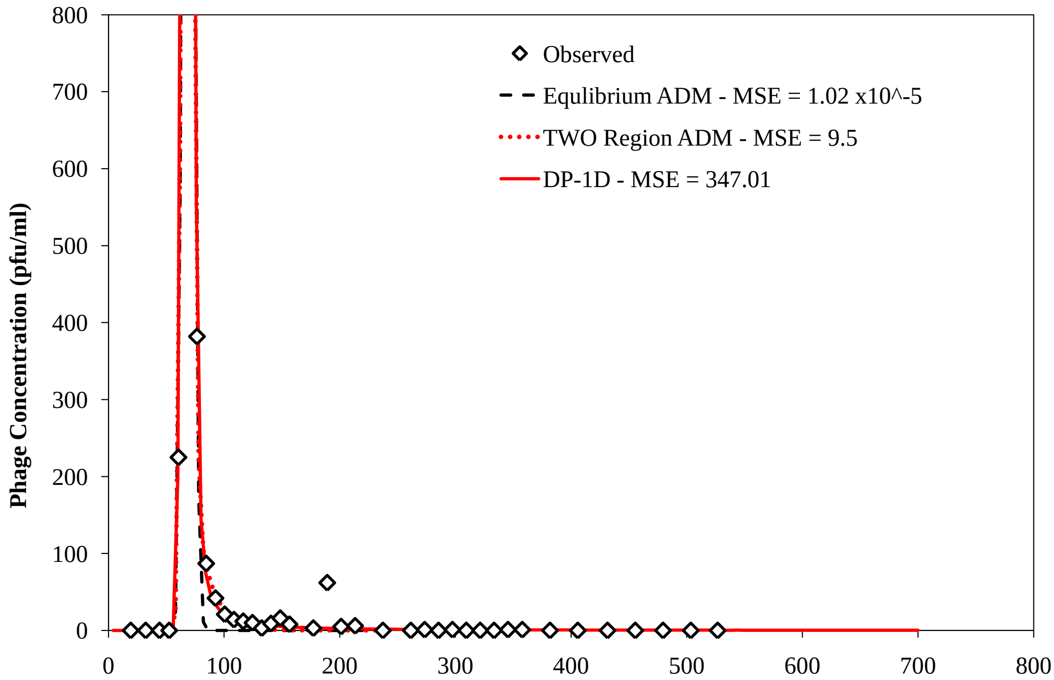


(b) Turnford PWS

Figure 6.7: Non-uniqueness problems in fitting models to some breakthroughs where there is insufficient data to define the initial breakthrough and thus transport velocity. The short duration of the rising limb of breakthrough and the apparent tailing in the falling limb of the breakthrough suggest it is most likely that observations at low frequency sampling points occurred on the falling limb of the tracer tail. The two region and DP-1D models provide the most likely simulations of tracer breakthrough and show similarity in form to the Qtracer2 type curves for Essendon PWS, Arkley Hole Spring and Lynchmill Spring.



(a) Essendon PWS



(b) Arkley Hole Spring

Figure 6.8: Fitting of a two region advection dispersion model with CXTFIT and Dual porosity diffusion model using DP-1D to tracer breakthroughs from Water End at Essendon PWS and Arkley Hole PWS.

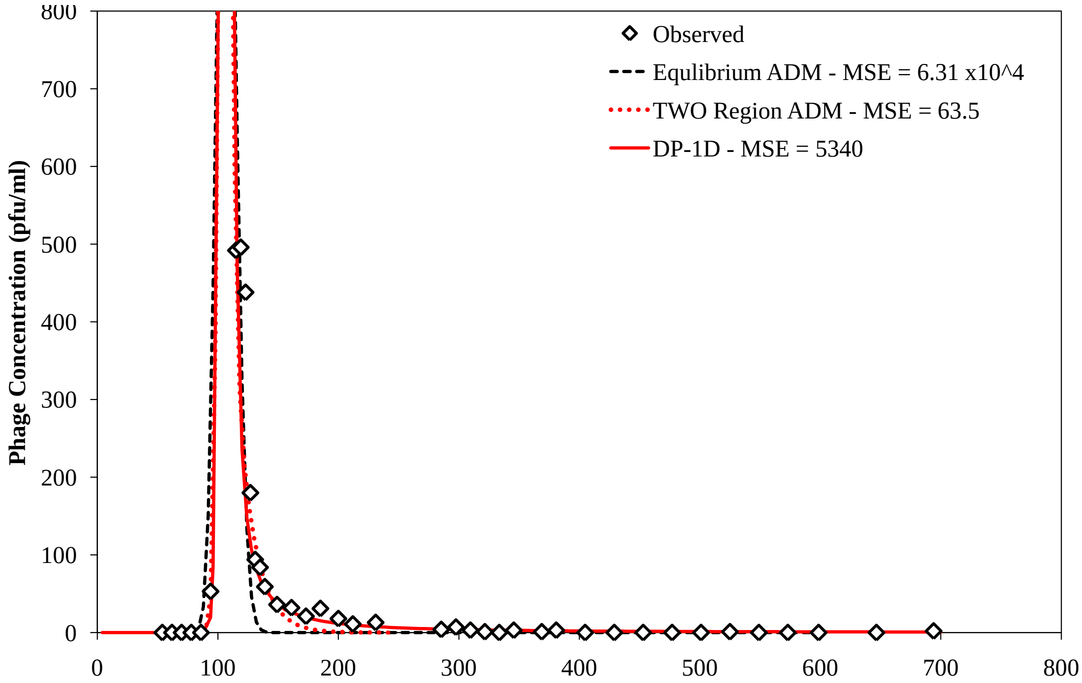


Figure 6.9: Fitting of a two region advection dispersion model with CXTFIT and Dual porosity diffusion model using DP-1D to tracer breakthroughs from Lynchmill Spring.

Tailing of tracer breakthrough curves is a commonly observed phenomenon and is generally considered to represents some form of temporary storage and slow release of tracer by various mechanisms including temporary sorption, matrix diffusion and temporary entrapment in immobile or stagnant flow zones. The analytical modelling approaches adopted have demonstrated comparable fits to the Tracer breakthrough curves of both a two region model and a fully diffusive matrix exchange model with comparable goodness of fit highlighting an issue of non-uniqueness of solutions to the data. In one sense, this might be expected since the quasi steady state (QSS) method of solution used within CXTFIT2 is sometimes considered to be an approximation of the explicit diffusion based approach of the DP1D code (Barker, 2005) and the QSS method is often adopted to approximate dual porosity conditions in complex finite difference groundwater transport models (e.g. MT3D-MS (Zheng and Wang, 1999)). However, the underlying assumption and conceptual models of the two methods are different: DP-1D explicitly assumes that the additional tailing is caused by Fickian diffusion between the mobile and immobile porosities whilst the QSS effectively represents a partitioning of the tracer to any immobile region such as micro fractures, dead end conduits or fractures and not just by diffusion into the primary porosity.

Massei et al. (2006) who also analysed tracer breakthroughs using Qtracer2 suggest that tailing in karst conduit systems could alternatively be due to additional dispersion introduced by turbulent flows within the conduit system and successfully analysed a tailed tracer breakthrough in karstic Chalk using two complimentary advection dispersion models; an initial rapid turbulent breakthrough and a slower friction dispersed breakthrough. However, the system studied by Massei et al. (2006) comprised a sink and source probably joined by a single conduit and hence the methodology may not be applicable to this test where multiple dispersive conduits distribute transport.

In the Chalk aquifer it is possible that both diffusion and other physical dispersive processes may be operating simultaneously. Maurice (2008) suggests that phage would behaviour as particulate tracers and would not participate in diffusive processes and that it would be inappropriate to incorporate such in models of their breakthrough. However comparison of the phage size, ($\approx 20 - 50nm$) with that of chalk pore throats ($\leq 1\mu m$) suggests that diffusive exchange of phage with the chalk matrix by Brownian motion, if not by differential concentration gradient, is at least physically plausible.

A further consideration is of the characteristic times given by the DP-1D method, the overall duration of tracer observation is most consistent with that of the mean advection time, t_a, and is shorter than the fracture equilibrium time t_{cf} and vastly shorter than that for equilibrium across the matrix blocks t_{cb}. The transport suggested by the tracer breakthrough curves suggests that the significance of diffusion is limited in those locations that show tailing, although limited diffusion could occur and can account for the observed tailing. The implication of low t_a and high t_{cf} is therefore of advection dominated rapid transport in large aperture features consistent with a karst conduit system. That advection dominates in the karst system, and the role of diffusion is relatively insignificant, is further illustrated by the Peclet numbers derived from the Qtracer2 model (table 6.5).

The estimation of a first order mass transfer coefficient ω by the CXTFIT and DP-1D models provides an indication of the magnitude of partitioning of solutes between mobile and immobile zones. The general form of the partitioning equation for dual porosity exchange is:

$$\theta_{im}\frac{\delta C_{im}}{\delta t} = \omega(C_m - C_{im}) \tag{6.1}$$

Where θ_{im} is the immobile porosity, C_{im} is the immobile phase concentration, C_m the mobile phase concentration and ω is the mass transfer coefficient. The values of ω derived from the tracer breakthrough curves very small, on the order of 1×10^{-5} to 1×10^{-8} and are again suggestive that the role of the immobile zones and/or the chalk matrix in limiting concentrations within the karst flow system is minimal.

Although there is insufficient evidence to completely discount a dual porosity diffusive signature on the tracer breakthrough curve, since the two region model is less specific about the precise cause of the tailing, the fitted parameters from this method will be adopted for transport modelling of bromate in the Hertfordshire Chalk karst system. Furthermore since the method is the same as that used for finite difference transport models, these parameters are consistent with such an approach.

Table 6.9: Estimates of equivalent plane parallel fracture apertures for the 2008 tracer test using the cubic law approach

	Aperture (mm)		
Location	Harefield House Injection	Comet Way	Water End
Hatfield Quarry WM12	0.76	-	-
Hatfield PWS	-	-	3.17
Essendon PWS	2.16	2.66	3.33
Arkley Hole Spring	2.90	4.69	4.91
Lynchmill Spring	3.71	1.92	4.80
Amwell Marsh PWS	-	-	4.04
Rye Common PWS	-	-	4.08
Turnford PWS	-	-	3.26

6.2.2 Estimation of Conduit Apertures

The size of the conduits is another important parameter in characterising the system since this influences the proportion of flow which can be carried and also influences if flows are laminar or turbulent. (Maurice et al., 2006) gave field observations of chalk conduits in the range 0.2 - 1.0m in diameter.

The most commonly taken approach for tracer tests in the Chalk aquifer is to use to cubic law to estimate the aperture of an equivalent plane parallel fracture as was done in Chapter 4 for the tracer tests of (Harold, 1937). Estimates of fracture apertures using the same method are presented in table 6.9

The estimated apertures are similar to that for the 20th century tracer test which is not surprising given the close agreement in travel times between the 2008 tests and those of (Harold, 1937). The spring locations show the largest equivalent apertures fractures and apertures appear to decrease in aperture with distance from the Palaeocene boundary which is consistent with weathering and infilling of less active features (or the increased enhancement of such features at the boundary). However, adoption of the plane parallel fracture approach is probably inadequate and unrealistic since field data seems to suggest that there is a well developed network of karst conduits dominating transport rather than a fracture system.

A simple approach for estimating conduit diameters is described by (Field and Nash, 1997) and if the conduit discharge (Q) and mean flow velocity (v) are known, the volume of the conduit (V), and therefore the diameter of the conduit can be estimated (Equation 6.2) assuming a cylindrical form along the flow path length (L).

$$V = Q\frac{L}{v} \tag{6.2}$$

The required data can be estimated for the spring locations by taking the mean groundwater velocities from Table 6.7 and the flow path lengths from Table 6.1 The discharge has assumed to that estimated during the tracer tests (130l/s and 30l/s for Arkley Hole and Lynchmill Spring respectively). Using these discharge data a conduit aperture of 1.08 and 0.49m is estimated are for Arkley Hole Spring and Lynchmill Spring respectively. The discharge of conduits connected to wells cannot be determined since the well pumped discharge probably incorporates a fracture component as well as that of any conduit(s).

However, (Birk et al., 2005) note that this method will tend to overestimate conduit diameter since it assumes one dimensional flow from swallow hole to spring and ignores the contribution of other flows (e.g fracture flow) to the spring or conduit system. Such additional contribution must be occurring in Hertfordshire since the spring locations show concentrations of bromate and must at least be receiving groundwater derived from further east in the catchment, and from the conduit arrangement and distribution of surface karst inputs from other swallow holes probably occur. The conduit estimates by this method therefore provide an upper boundary to the actual conduit diameter.

A possible refined estimate can be obtained by using the tracer recovery data to infer the proportion of flow entering the Water End swallow hole complex that arrives at the spring locations. The input into the water end swallow holes for the period 2005-2006 was derived by (Atkins, 2006), assuming the tracer test was undertaken at typical (average) conditions of approximately of this inflow would be apportioned to Arkley Hole Spring and Lynchmill Spring respectively. This gives diameters of 0.28 and 0.077m for Arkley Hole Spring and Lynchmill Spring respectively and much smaller than that for the full discharge approach.

Since the estimates of spring discharges for Arkley Hole and Lynchmill Spring during the tracer test are relatively crude, estimates of conduit aperture can be better constrained by use of more reliable data. The 2008 tracer test and those of Harold (1937) have indicated that the flow velocities within the Hertfordshire Karst system are consistent over a range of conditions and input locations. Limits to the discharge within the conduit system can therefore be imposed from the maximum recorded inflow to a swallow hole or discharge from a spring, which can then be used with the fastest observed conduit flow velocity data to determine a cross sectional area of flow required and thus an estimate of likely upper limits to conduit diameter. The maximum discharge and flow velocity and the corresponding maximum likely conduit diameters assuming a circular cross section for various locations are presented in Table 6.10.

The apparent flows within the conduit system can therefore be accommodated, in principal, by a single conduit not more than 2.1m in diameter, which is towards the upper of, but not unrealistic for observed diameters of Chalk cave and conduit systems (e.g Waters and Banks, 1997; MacDonald et al., 1998; Maurice et al., 2006; Edmonds, 2008). The 2.1m diameter estimate is derived from flows entering the entire swallow hole complex at Water End, although it is not inconsistent with anecdotal evidence of conduit size from cave exploration at the site, the complex does comprise a number of discrete swallow holes it is unlikely this flow is absorbed by a single conduit and some proportion of flow may also be lost to the fracture

Table 6.10: Estimates of the likely maximum aperture of conduits based upon maximum recorded discharges and flow velocities

Location	Maximum Flow (m^3/s)	Maximum velocity (m/s)	Minimum Equivalent Conduit Diameter (m)	Data source
Water End	1	0.068	2.1	Maximum capacity from Walsh and Ockenden (1982)
	0.254	0.068	1.07	Flow rate before complex begins to overflow to Colne in Atkins (2006)
Welham Green Bourne	0.17	0.068	0.89	Maximum gauged flow (Atkins, 2006)
Catherine Bourne Swallow Hole	0.043	0.037	0.61	Maximum flow rate recorded before bypass occurs (Atkins, 2006)
Arkley Hole Spring	0.16	0.037	1.17	Maximum gauged flow (Atkins, 2006)
Chadwell Spring	0.261	0.061	1.17	Maximum gauged flow (Newton, 2005*a*)
Emma's Well Spring	0.15	0.066	0.85	Whittaker (1921)
Lynchmill Spring	0.3125	0.059	1.30	Whittaker (1921)

system. The actual conduit diameter will therefore probably be lower than this estimate. Spring discharges also appear to occur from a number of discrete outflows rather than a single upwelling, again suggesting more than one conduit may be responsible for discharge. Actual observations of chalk conduits suggest a typical diameter is < 0.5m (Maurice, 2008) and given that the estimated data probably represent overestimates, conduit diameters of < 1m are feasible for Hertfordshire.

For the range of karstic flow velocities observed in the Hertfordshire tracer tests (0.022-0.068m/s) turbulent flows (where $R_e \geq 2300$) would occur above a conduit diameter of 0.04-0.13m, therefore the majority of karst flows within the conduit system are expected to be turbulent and would best be modelled by the Darcy Weisbach equation (Equation 4.7).

6.2.3 Summary of derived transport parameters

Analysis of the tracer breakthrough curves has yielded new information describing the transport properties (Table 6.11) of the Hertfordshire Chalk karst system which can be used to improve current models of the transport of bromate within the aquifer. Flow velocities are rapid and consistent with other carbonate conduit systems worldwide, dispersion and attenuation of contaminants within the conduit system is low which increases the impact of the bromate contamination at locations east of Hatfield. The connection of the karst system to these locations also increases their vulnerability to other contamination events that might intersect the karst system and the connections are not presently incorporated within the Environment Agency groundwater source protection zones for affected locations.

Table 6.11: Estimated range of transport parameters determined for the Hertfordshire chalk karst flow system. Parameters have been defined using the Water End injections only since these provide direct input into the karst system. Velocity data have been incorporated from the 20th Century tracer tests of Harold (1937) as well as the 2008 test. ^{a}st Dispersivity is taken from estimates for the spring locations.

Flow Velocity (m/s)	$\bar{v}$	0.0418
	σ_v	0.0145
Dispersivity (m)	Mean	24.47
	σ_d	15.58
Mass Transfer Coefficient	Minimum	1.15×10^{-8}
	Mean	9.92×10^{-6}
	Maximum	3.04×10^{-4}
Conduit Diameter (m)	Minimum	0.07
	Mean	0.96
	Maximum	2.1
Sinuosity		1.34

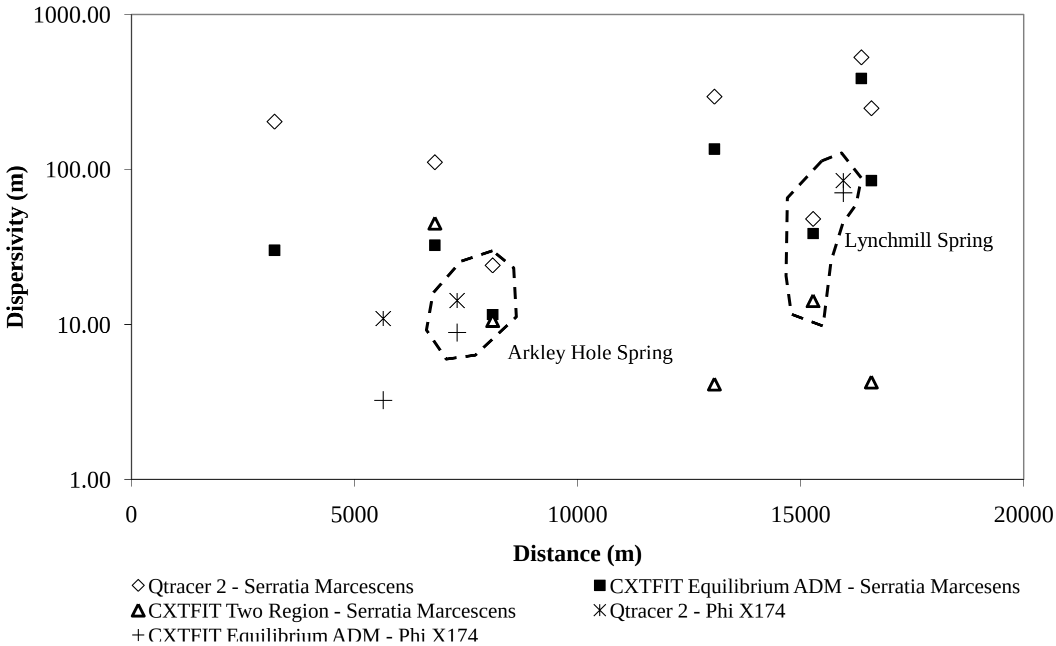


Figure 6.10: Variation of dispersivity with apparent straight line transport distance

The variation in dispersivity estimates for each model and with apparent straight line transport distance is presented in figure 6.10. Although there is variation between the estimation methods, the general pattern indicates a slight increase in dispersion with distance. Spring locations indicate a narrower range of variation and also have generally lower dispersivity than the PWS locations probably reflect their direct connection to the karst system.

6.3 Regional and Karst Water Budget

The groundwater flow system of the Hertfordshire Lee Chalk catchment is comprised of a diffuse chalk fracture-matrix system with a superimposed catchment scale karstic flow system. The karst flow system has been shown to be a important influence upon the transport of bromate, particularly to locations in the Lee Valley. There have been a number of previous attempts to determine a water budget for the Lee Catchment (e.g. Ingles, 1993; Entec, 2000; Buckle, 2002). However, in each case the defined catchments, and as a result the overall budgets, differ and so direct comparisons are not possible. Estimation of the karst input from the Water End complex and/or the Mymmshall Brook have been incorporated in all previous budget estimates and are in the range 20-30Ml/day. However, none of the previous budgets have taken account of the other swallow hole catchments developed along the Palaeocene feather edge and so have not fully incorporated the entire karstic extent of the aquifer.

This section describes a new water budget developed for the catchment in order to attempt to delineate all the relevant karst sub-catchments and so estimate the full contribution of karst flows to the regional water resources.

The data available for determining such a budget are relatively limited, particularly so for the karst features of the catchments where flow estimates of sinking streams or spring discharges are either non-existent or based on very limited gauging. Only the Mymmshall Brook, Arkley Hole Spring and Chadwell Spring have been subject to long term gauging and for the Mymmshall Brook and Arkley hole such gauging (in Atkins, 2006) only covers a period of less than six months and does not include a summer period. Development of a long term water budget over the course of a given hydrological year is therefore not possible given presently available data. Instead, a relatively crude estimate of the water budget has been derived based upon daily average of flows, Although this does not fully account for seasonal variations it does provide some insight into the relative significance of flows.

6.3.1 Groundwater Boundaries

A schematic plan of the assumed boundaries to the Lee groundwater system is provided in Figure 6.11.

No-flow boundaries are assumed parallel to the flow lines between the Lee GW catchment and that of the Ver and Colne to the South and West and the Mimram to the North. A further North-South aligned no-flow boundary has been delineated along a flow line approximately parallel to the River Lee. All groundwater and recharge entering the sub-catchment of the Mymmshall Brook is assumed to be captured by the karst flow system and hence a further no flow boundary is delineated approximately by the outcrop of the London Clay in this area.

Groundwater inflow boundaries occur in the North west due to influx of groundwater sub parallel to the River Lee, and similarly in the north east for flow along from Mimram groundwater catchment and from the Rib and Beane catchments on the northern loop of the River Lee. The quantity of inflow across these boundaries has been calculated using Darcy's Law assuming a Chalk transmissivity for the Chilterns of $900m^2/day$ (see section 3.7.1) and the width of boundary. The hydraulic gradient

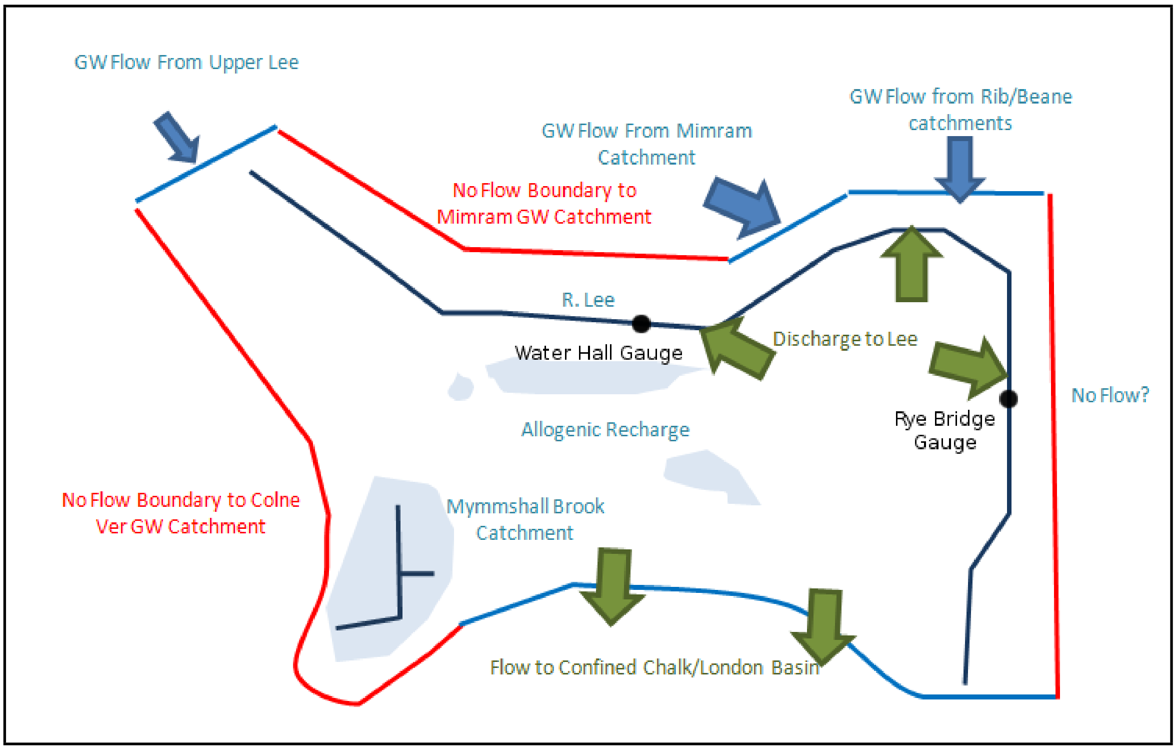


Figure 6.11: Schematic delineation of the extent and main boundaries of the Lee GW catchment

Table 6.12: Calculation of groundwater inflows and outflows using Darcy's law.

Boundary	Approximate Length (m)	Transmissivity (m^2/day)	Hydraulic Gradient (i)	Flow (Ml/day)
Inflows				
Upper Lea	5300	900	0.0020	9.5
Mimram	4500	900	0.0022	8.9
Rib/Beane	4800	900	0.0015	6.5
Total Inflow			24.9	
Outflows				
To confined chalk	12000	200	0.02	48

is calculated from the regional piezometry across the inflow boundary (see section 3.6).

A single groundwater outflow boundary is assigned along the southern extent of the groundwater catchment approximately aligned with the 10mOD piezometric contour and groundwater is assumed to flow southeastward across this boundary into the confined Chalk of the London Basin. Groundwater outflows were calculated in the same manner to inflows although a transmissivity for confined Chalk of 200m^2/day was adopted.A summary of the estimated groundwater inflows and outflows is presented in Table 6.12. The estimate of flow to the confined chalk of the London Basin agrees reasonable well with the water budget estimate of 50Ml/day by (Ingles, 1993) for the period 1985-1986.

6.3.2 Recharge

The catchment recharge incorporates both diffuse flow due to precipitation and the discrete allogenic recharge from sinking streams via swallow holes.

Data presented in Buckle (2002) suggest the long term average precipitation the area between 1920 and 1998 is 642mm/a and the associated average potential evapo-transpiration is 531mm/a. However actual recharge is complicated by other factors including leakage from sewage mains as well as variations with the geology and soil type. A stand alone run-off recharge model for the Hertfordshire Lee catchment was developed as part of regional groundwater model development (in Assem, 2005). This model incorporates differential recharge based upon soil and geological variations, topography, evapo-transpiration and sewage leakage and allows bypass flows to represent direct infiltration along the chalk fracture system through the unsaturated zone. For this relatively crude water balance the typical range for the chalk outcrop of 0.1-0.8 mm/day with a modal average of approximately 0.6mm/day, equivalent to 219mm/a Assem (2005) has been adopted. No recharge has been assumed to occur in the area underlain by the London Clay.

In assessing allogenic recharge only the Mymmshall Brook upstream of Water End (Average of 10.6Ml/day), Welham Green Bourne (4.5Ml/day) and the Catherine Bourne (1.5Ml/day) streams have been subject to any long term flow gauging by Atkins (2006) and also by earlier spot gauging by the Environment Agency within the Mymmshall Brook Catchment (Data provided by Atkins, 2006). No data are available for the other swallow hole catchments developed within the Mymmshall Brook catchment and elsewhere on the Palaeocene escarpment between Hatfield and Hertford. Gauged data for the Mymmshall brook has been assumed to be equal to the flow which reaches the Water End complex itself taken from the gauge at Abdale lane some 300m south of the complex.

Two methods have been employed to derive estimates of the inflow into non gauged swallow holes which both make use of the estimated catchment sizes (Figure 6.3). The first method takes the average flow to swallow holes for each of the three gauged swallow hole catchments to determine an average flow per unit area of the catchment (which are $2.36 - 8.27 \times 10^{-7}$Ml/m^2 per day). This rate is then applied to each swallow hole catchment on a pro-rata by area basis to estimate the likely range of recharge. This method assumes that the runoff reaching the swallow holes is based upon similar climatic conditions, land surface cover, topography and vegetation in each swallow hole catchment to those of the gauged swallow holes. Given the proximity of the swallow hole catchments and their common position on the Palaeocene escarpment this is probably a reasonable assumption.

The second method makes use of the precipitation rate (638mm/a) and potential evapo-transpiration rate (540mm/a) described above and assumes that the net recharge (102mm/a) for each swallow hole catchment enters the conduit system

Table 6.13: Estimates of diffuse and allogenic recharge for the water budgeting area

Component	Catchment Area (m^2)	Average Flow (Ml/d)	
Diffuse Recharge	1.78×10^8	106.8	
Gauged Swallow Holes			
Mymmshall Brook at Water End	4.5×10^7	10.6	
Welham Green Bourne at Water End	5.5×10^6	4.5	
Catherine Bourne	5.2×10^6	1.5	
Swallow Hole Estimates		**Pro-Rata Method**	**Areal Recharge Method**
Potwells	5.57×10^4	0.025	0.015
Gobions Wood	5.43×10^6	2.429	1.488
Other Mymmshall Brook Swallows	2.7×10^7	12.08	7.4
Hatfield Park	1.00×10^6	0.45	0.27
Howe Dell	2.80×10^6	1.25	0.77
Cuffley Brook	4.57×10^6	2.05	1.25
Brickkiln Wood	6.18×10^5	0.28	0.17
Popes Wood	1.20×10^6	0.54	0.33
Essendon Brook	7.00×10^6	3.13	1.92
Little Berkhamstead	4.60×10^6	2.06	1.26
Total allogenic recharge		40.88	31.47
Total Recharge		147.68	138.27

either by surface run-off into swallow holes or infiltrates into the chalk and the sub-surface karst. However, this approach ignores the possibility of bypass flows which are highly likely to occur in the swallow holes and hence will underestimate the actual recharge. A summary of the estimated recharge for the area is presented in Table 6.13.

The recharge estimates are consistent with other estimates of 123Ml/day ((Entec, 2001) in (Buckle, 2002)) and that of Buckle (2002) of 120.3Mlday. Catchment areas differ slightly between studies, for example the Entec (2000), Buckle (2002) and Ingles (1993) budgets incorporate the Mymmshall Brook catchment as part of the Colne catchment, which is strictly true for the surface water catchment but the groundwater tracing has shown it is likely that this flow enters the Lee GW catchment and has been incorporated as such for this accounting. The estimated contribution of recharge from the Mymmshall Brook catchment, i.e. the total flows from the Water End, Catherine Bourne, Mymmshall Brook, Potwells and Gobions Wood Swallow Holes is 25.2 - 31.1 Ml/day depending on the method chosen.

6.3.3 Spring Discharges

The major spring discharges, whilst not presently comprehensively gauged have been subject to spot or continuous gauging in the past. The range of flows used for the water budget estimation are presented in Table 6.14.

Table 6.14: Summary of spring discharges adopted for water budget calculation

Spring	Discharge (Ml/d)			Data Source
	Maximum	Minimum	Average	
Arkley Hole	11.0	0.0	6.0	Atkins (2006)
Chadwell Spring	10.0	0.0	5.0	Gauged data from Newton (2005*a*)
Lynchmill Spring	6.0	0.0	4.0	Whittaker (1921)
Emma's Well	4.0	0.0	2.0	Whittaker (1921)
Other Springs	10.0	0.0	4.0	Estimate
Total Discharge	41.00	0.00	21.00	

Table 6.15: Calculation of estimated groundwater discharge to the River Lee between Water Hall and Rye Bridge.

Flow Component	Long term Average Flow (Ml/d)
Gauge at Water Hall	107.1
Mimram tributary at Panshanger	43.3
Beane Tributary at Hartham	43.6
Rib Tributary at Wadesmill	25.1
Abstraction at New Gauge	-86.4
Ash Tributary at Mardock	25.1
Calculated flow at Rye Bridge	158.2
Actual flow at Rye Bridge	244.1
Assumed Groundwater Contribution	85.9

6.3.4 Flow Outputs to the River Lee

Estimates of groundwater discharge to the River Lee can be derived from flow gauging data provided in Atkins (2006). The River is gauged at two locations within the area of interest, the locations of which are shown in Figure 6.11. According to Buckle (2002) the River is perched on the Lowestoft Till north and west of approximately the position of Arkley Hole. Downstream of this location the Lee is assumed to be effluent and in communication with groundwater until it crosses the boundary of the London Clay in the Lee Valley.

Groundwater discharge to the River Lee in the effluent reach has been estimated by addition of the gauged flows of all tributaries at their closest gauged point to the Lee to that of the gauged flow in the Lee at Water Hall, which includes the contribution of Arkley Hole. The average TWUL abstraction from the Lee into the New River for the period 2004-2008 at New Gauge has been subtracted from the total and the estimated flow is then compared to the measured flow at Rye Bridge and the difference in the two flows has been taken as the contribution of groundwater. This accounting is summarised in Table 6.15.

There are considerable uncertainties with this approach, for example it does not include the possibility of additional surface water run-off entering the Lee or its tributaries downstream of the gauged locations. It also ignores the possibility of further abstraction, and discharge downstream of New Gauge, therefore attributing all the gain in flow along the reach probably overestimates the groundwater contribution.

It also ignores the possibility of groundwater flow entering the River Lee upstream of Water Hall gauge station or downstream of Rye Bridge, although the

Table 6.16: Summary of abstraction data used to calculate water budget. The adopted values are based on 2008-2009 abstraction patterns

Location	Abstractions (Ml/d)			
	Maximum	Minimum	Average	Adopted
VWTV Abstractions				
Hatfield PWS	9.20	0.00	6.01	6.00
Tyttenhanger PWS	8.80	0.00	6.20	6.20
Roestock PWS	8.70	0.00	6.40	6.40
Essendon PWS	10.10	0.00	6.60	4.00
Water Hall PWS	1.40	0.00	0.60	0.60
Wheathampstead PWS	6.60	0.07	3.40	3.40
Shakespeare Road PWS	3.80	0.00	1.80	1.80
TWUL Abstractions				
Broadmeads PWS	8.40	0.00	2.00	0.00
Amwell End PWS	5.60	0.00	2.30	0.00
Amwell Hill PWS	16.50	0.00	4.70	0.00
Amwell Marsh PWS	30.00	7.90	17.50	20.00
Rye Common PWS	21.20	0.00	11.50	18.00
Hoddesdon PWS	18.70	0.00	7.40	0.00
Middlefield Road PWS	3.00	0.00	0.04	0.00
Broxbourne PWS	15.80	0.00	7.10	0.00
Turnford PWS	10.80	0.00	4.20	2.00
Private Abstractions	45.50	0.18	9.80	10.00
Total Abstraction	224.10	8.15	97.55	78.40

presence of extensive drift including brickearth and till south of Rye Bridge may limit the groundwater contribution in this reach. Between Water Hall and the upstream gauging location at Luton Hoo on the north western boundary of the water budget accounting area, the flow in the River Lea increases by approximately 86.8 Ml/day. A few tributary streams do occur draining the Palaeocene escarpment to the south although these catchments are drained by swallow holes and hence their contribution may be limited except during heavy flows. Arkley Hole Spring accounts for an average input into the river of 6Ml/day as assumed above. Major water treatment work discharges occur at Mill Green and East Hyde and are thought to account for much of the observed increase (Buckle, 2002). The contribution from groundwater over this length is thought to be relatively low although springs associated with the Chalk Rock occur at Batford, Wheathampstead and Lemsford.

6.3.4.1 Groundwater Abstractions

Groundwater abstractions can be split into two groups, those for public supply and those for private use including residential, agricultural and commercially operations. Mean daily abstractions by month for the period 1970-2004 are provided by (Assem, 2005) and have been used to derive long term daily average abstraction rates for the private abstractions. The actual pumping regime of the public abstraction wells can be better constrained, particularly since the emergence of the bromate problem and the operation of Hatfield PWS as a scavenging borehole and the recent abstraction patterns have been adopted for public water supply locations. A summary of the groundwater abstraction data are presented in Table 6.16.

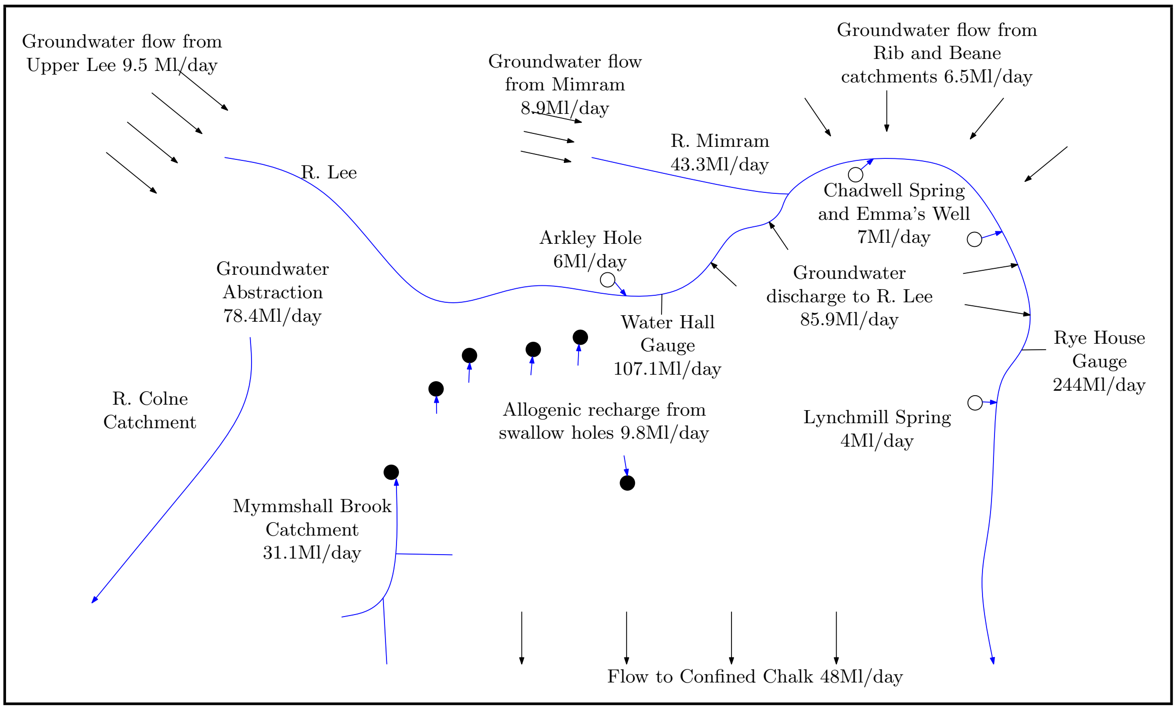


Figure 6.12: Summary of the Lee GW catchment water balance

6.3.5 Overall Balance Estimate

The estimated long term average daily water balance is provided in Table 6.17 and Figure 6.12.

The deficit of 60.7Ml/day can in part be accounted for by the likely overestimate of groundwater discharge to the River Lee and the probable underestimate of the karst recharge as well as the errors in calculation and estimation of other flow components. A small net deficit may even be appropriate under long term conditions given the stressed nature of the aquifer.

On average the allogenic karst recharge is estimated to contribute approximately one third of the total recharge to the catchment, however the actual contribution

Table 6.17: Summary of Water Budget account for the Lee GW catchment. * The higher value obtained using the pro-rata method has been adopted since it is likely that the catchment area method produces an underestimate

Component	Average Flow (Ml/dy)	Proportion of flow (%)
Inputs		
Diffuse Recharge	106.8	61.9%
Allogenic Recharge*	40.9	23.7%
Groundwater Inflows	24.9	14.4%
Total In	172.6	100
Outputs		
Abstractions	78.4	33.6%
Karst Spring Discharge	21	9.0%
Loss to River Lee	85.9	36.8%
Flow to Confined Chalk	48	20.6%
Total Out	233.3	100%
Deficit	60.7	24.3% of outflows

might be greater during heavy flows where the gauged flow at Water End has been estimated to reach up to 86Ml/day (Walsh and Ockenden, 1982) and large flows probably also occur at other swallow hole catchments. Conversely flow contribution during dry periods may be minimal since many ephemeral swallow hole catchments (particularly the smaller ones developed on the Palaeocene outcrop) are dry during periods of low rainfall. Despite being a large and probably seasonal contribution to the overall water budget since the flows through the karst system are known to discharge to the Lee valley springs rapidly the long term contribution to the total available water resources may be limited except during conditions where there is sustained flow to the swallow hole systems (for example during the winter). It has been postulated (e.g. Buckle, 2002; Assem, 2005) that such a mechanism may be responsible for the apparent seasonal response of Bromate concentrations observed at Essendon PWS and at the NNR wells.

Estimates of the major spring discharges account for less than half of that estimated to be input direct to the karst system suggesting the remainder is either transmitted to the fractured aquifer or is discharged through other outflows, perhaps in the base of the River Lea. At least part of the remainder is abstracted from wells that are linked to the karst system although this proportion cannot be easily quantified without further tracing and gauging work.

Brown and Ford (1971) and Atkinson et al. (1973) suggest five types of karst flow network dependent upon the relative proportions of inflow and outflow and the recovery of tracer mass (figure 6.13). Since the discharge from the springs is somewhat less than that of the estimated karst inflows and the tracer recovery is much less than that injected it is likely that the Hertfordshire karst corresponds to a type 4 network with both tributary swallow hole systems and distributary conduits to a number of springs and also discharge to abstraction wells. Additional tributary flow into the karst system also occurs from the diffuse fracture flow.

Although this water balance makes some further progress towards identifying the proportion of flows within the system, neither the tributary flows from the diffuse fracture system nor the volume of karst discharge to abstraction wells can be easily constrained. It is likely that both are variable with dependency on a number of factors including water levels in the aquifer, recharge and abstraction rates.

6.4 Evolution of the Karst System

Having established the function of the karst system, the following section postulates how the system may have evolved and based upon the interpreted flow regime and the geomorphological and geological context of the region.

The conceptual model for the formation of karstic conduits and solution enlarged fractures in the Chalk aquifer presented by Maurice et al. (2006) classified the terrain

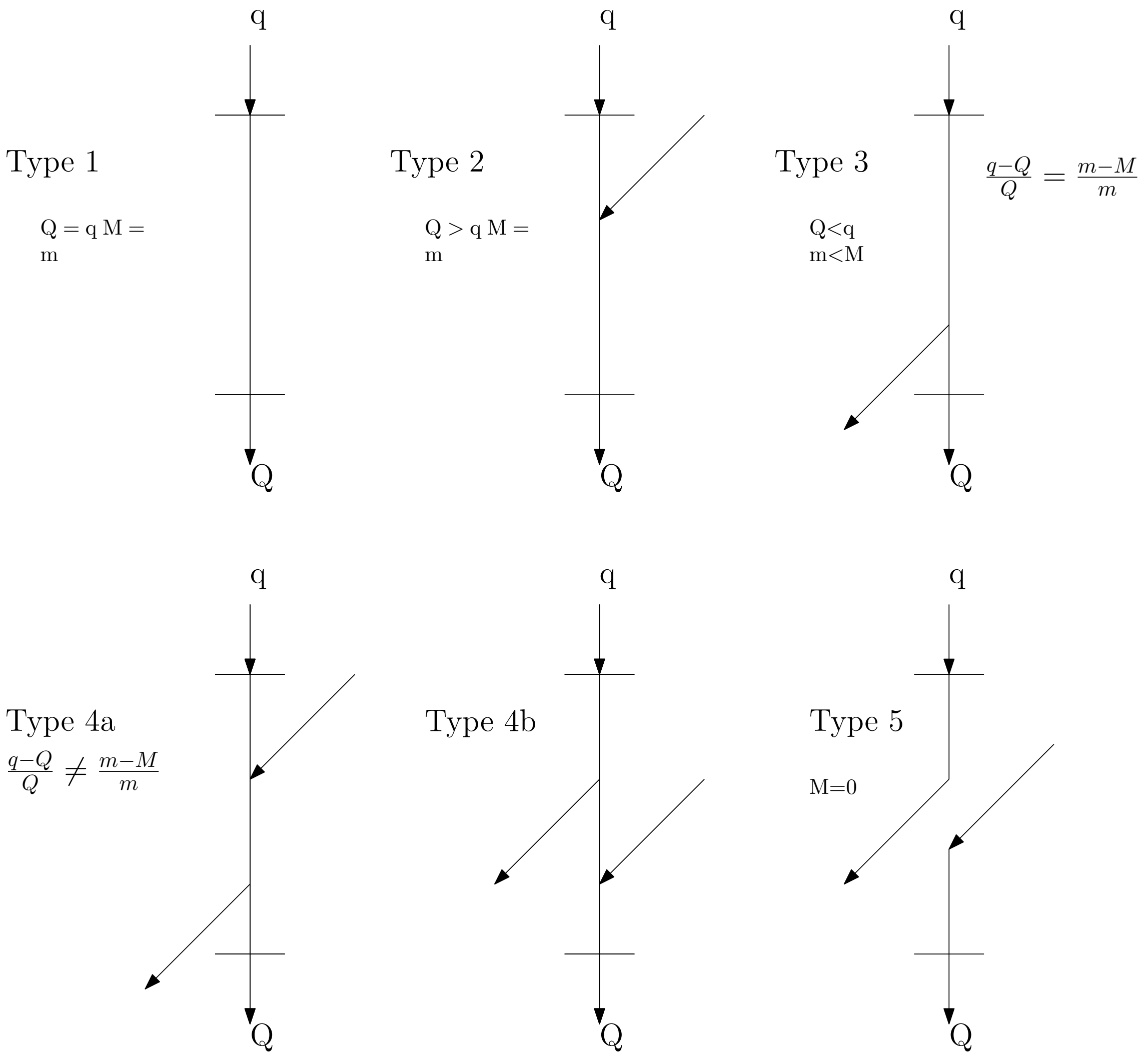


Figure 6.13: Possible arrangements of karst flow networks after (Brown and Ford, 1971) and (Atkinson et al., 1973). q = swallow hole discharge, Q = spring discharge, m = tracer input, M = tracer recovery. The Hertfordshire karst most closely corresponds to a type 4a network with tributary flow from the diffuse fractured aquifer and distributary discharge to abstraction wells and other locations including base flow to the River Lee

and occurrence of surface karst into three geomorphic zones based upon the distribution and hydrogeological significance of the Chalk karst features. It is not possible to directly apply this conceptual model to the area of interest Hertfordshire since the geomorphological evolution of the region has been complicated by the evolution of the Proto-Thames drainage system and the subsequent Anglian glaciation of the Vale of St Albans which is likely to has led to extensive denudation and excavation of the boundary between Zone 1 and Zone 2 as defined by Maurice et al. (2006).

Figure 6.14 delineates the approximate boundaries of the geomorphic zones as was applied to the Berkshire Chalk. Zone 1 is present in a broadly similar but slightly modified state being on higher ground (The South Hertfordshire Plateau) and thus forming the upper reaches of tributary catchments of the River Lee and Colne, for example the Mymmshall Brook and Cuffley Brook which contain stream sinks which are considered to feed conduits and solution-enlarged fractures which drain to the north-east into the Lea Valley. Further east, Zone 1 also includes the lower reaches of the River Lee and includes the Lee Valley springs. This area is characterised by a high degree of sub-surface dissolution.

Zone 2 has been truncated by the glaciation of the Vale of St Albans and erosion in the River Valleys of the Proto-Thames and more recently the River Lee. Thus the Proto-Thames and Anglian glaciation have directly impacted the evolution of the area across the Palaeocene-Chalk boundary, and as a result the area of most concentrated karst development.

To the northeast of the Vale of St Albans the geomorphology is more consistent with Zone 2 described by Maurice et al. (2006) although dip-slope dry valleys appear common. Ephemeral discharges occur, such as the flooding observed in the Sandridge dry valley. Minor springs associated with stratigraphic features such as at Lemsford and Wheathampstead also occur. There remains potential for some surface and sub-surface karst associated with the Clay-with-Flints which caps hills in this area although none has presently been mapped.

6.4.1 Prior to the Anglian Glaciation

During the Lower and Middle Pleistocene (figure 6.15) the Proto-Thames occupied the Vale of St Albans flowing approximately WSW-ENE. Initially at least, the Proto-Thames may have flowed above the Palaeocene outcrop since the Vale splits the main Palaeocene escarpment in the south east from the Clay-with-Flints and Foundered Palaeocene outcrop in the north west. Additional evidence for this is provided by the occurrence of Kesgrave Sands and Gravels above the Lambeth Group and London Clay as well the distribution of the Pebble Gravels above the London Clay which are thought to have originated in tributaries to the Proto-Thames and contain material derived from the London Clay and Lambeth Group.

Exposure of the Chalk within the Vale of St Albans, and therefore the possibility of erosion and dissolution of the rock occurred must have occurred at some point during the initial deposition of the Kesgrave Catchment gravels (forming the Westwood and Westmill units (Gibbard, 1977). Deposits of this group are also associated with the Valleys of the Lee and Mimram and could suggest early versions of these rivers acted as minor tributaries to the Proto-Thames as also indicated by a north-south aligned tributary along the modern Lee Valley.

Although there is little known surface karst to the north and west of the Vale, since the Clay-with-Flints represents foundered and solution/cryoturbation weathering of Lambeth Group deposits, there is a strong likelihood that such features do exist beneath and adjacent to this unit. Elevation of the Clay-with-Flints unit north of St Albans might be indicative of the likely elevation of dissolution features in this area northwest of the Vale of St Albans. Both the Palaeocene and the Clay-with-Flints appear to be relatively flat-lying closely following the 120mOD topographic

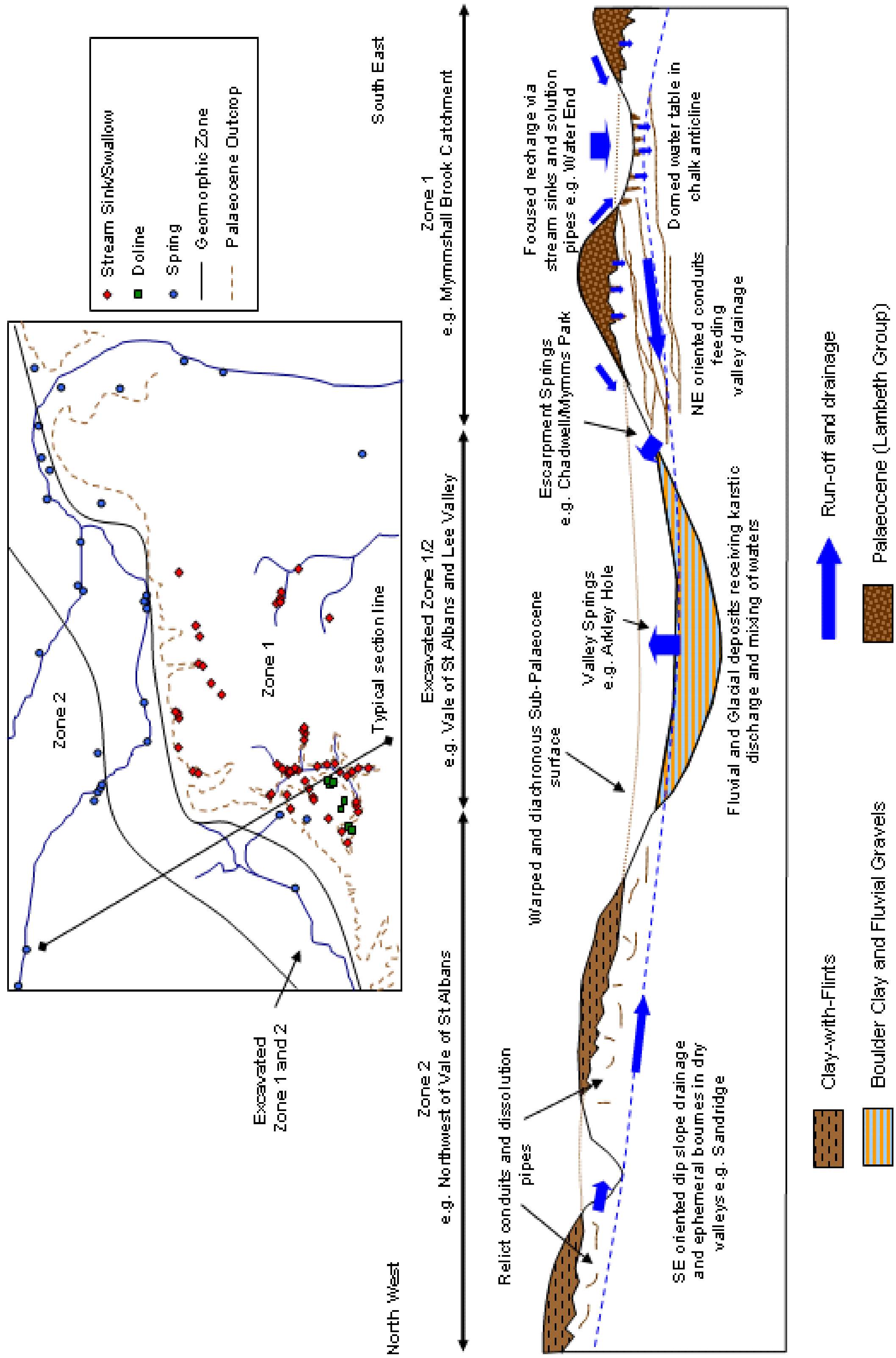


Figure 6.14: Zonation and schematic cross section of the Hertfordshire Chalk karst based upon the conceptual model of Maurice et al. (2006)

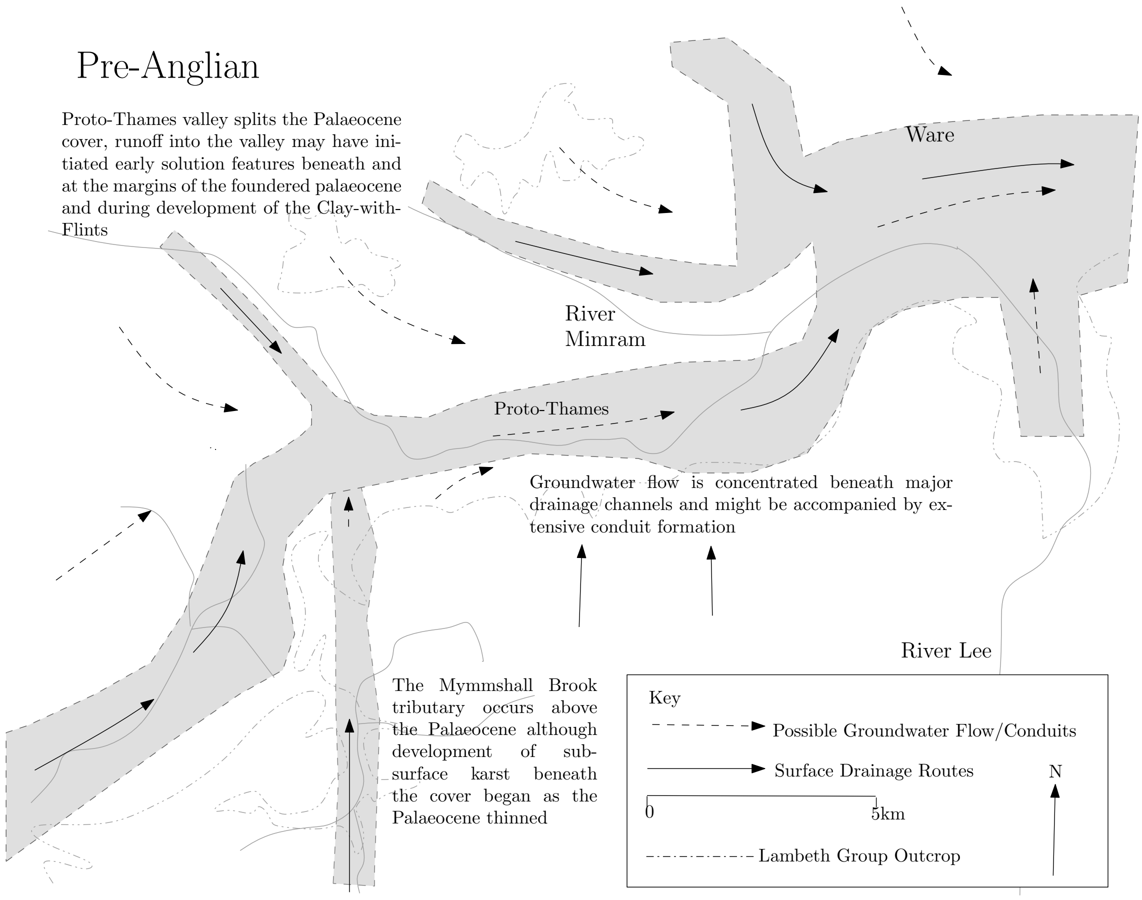


Figure 6.15: Inferred distribution of surface and subsurface drainage routes (grey shading) during the Lower to Middle Pleistocene period. The surface drainage roots (excluding that of the Mymmshall Brook) are from Gibbard (1977); Bridgland and Gibbard (1997)

contour. Soliflucted Clay-with-Flints appear below this elevation to about 100mOD. There is a drop in elevation of Chalk-Palaeocene boundary across the Vale of St Albans of approximately 30m probably due to the south-westerly dip. Ground levels in the Vale of St Albans are approximately 80mOD, indicating at least 20 to 30m of Seaford Chalk must have been removed by the Proto-Thames and incorporating the thickness of Proto-Thames and glacial deposits (approximately 15-20m (Gibbard, 1977)) suggests up to 40m of Chalk removal.

Widespread dissolution of the Chalk probably originated during this period once the Palaeocene cover had been breached or sufficiently thinned to allow infiltration and flow beneath the acidic Palaeocene and/or Clay-with-Flints into the Chalk outcrop of the Vale of St Albans. Conduits may have developed sub-parallel to the major valley axes and in particular beneath the Proto-Thames following a SW-NE alignment. It is possible the peri-glacial mechanisms discussed by Younger (1989) for the Devensian Proto-Thames may have contributed to conduit formation, although in this area of Hertfordshire suitable conditions may have existed earlier. Initial swallow holes and sink holes might have developed along the margins of the Palaeocene deposits on either flank of the Vale during this time and may have contributed flows feeding into the Proto-Thames valley.

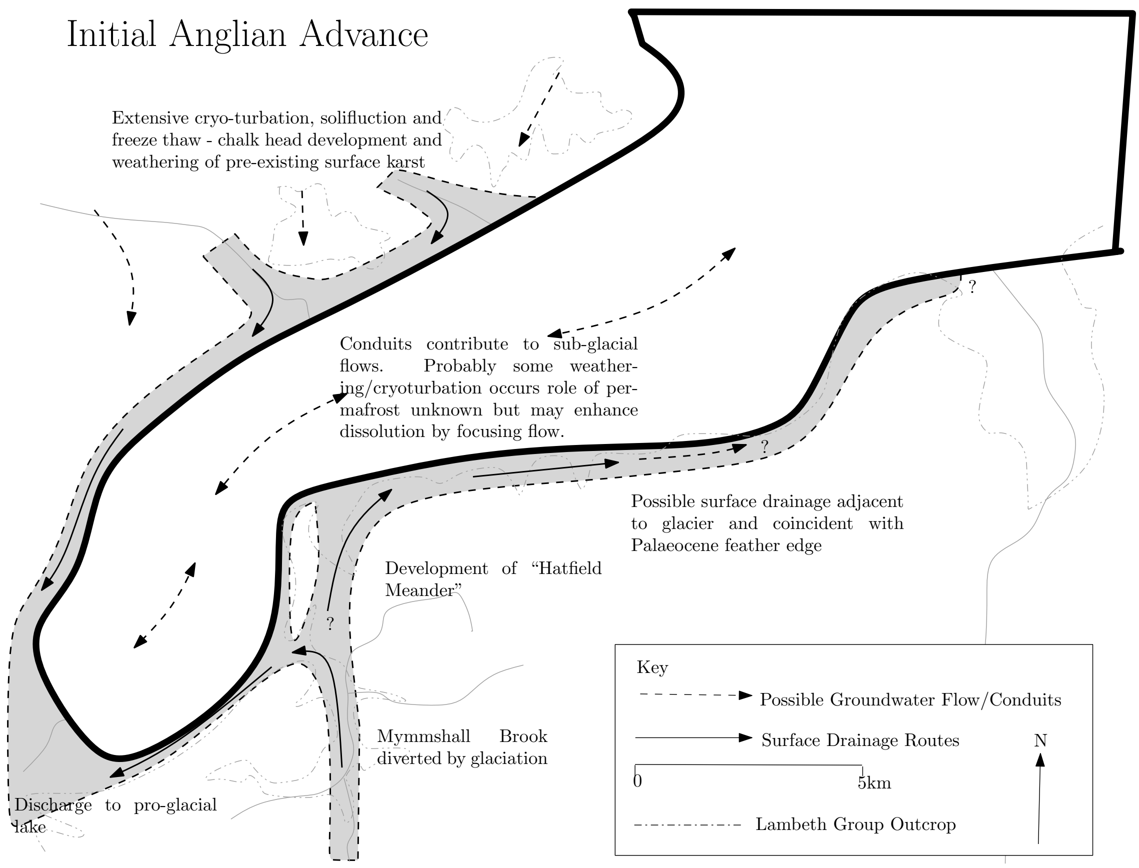


Figure 6.16: The first major Anglian ice advance (bold line). Surface and sub-surface drainage may have continued parallel to the Vale axis adjacent to and beneath the glacier. Groundwater flows may have switched toward the pro-glacial lake or have continued along the previously establish route towards the north east. The distribution of ice, surface drainage roots (excluding that of the Mymmshall Brook) are from Gibbard (1977); Bridgland and Gibbard (1997)

6.4.2 The Anglian Glaciation and subsequent evolution

The Anglian glaciation occurred in several stages from approximately 470,000 M.a. (Sumbler, 1996), initially the glacial advance was limited and short lived reaching as fare as Ware and possibly further south along the Proto Mole-Wey. Apart from forming a small pro-glacial lake in the vicinity of Hertford (Gibbard, 1977), the impact upon the surface, and therefore sub-surface drainage was limited and the Proto-Thames continued to flow without diversion, possibly during, but certainly after retreat of the initial ice advance.

The main glaciation (Figure 6.16) extended south west along the Vale to at least the St Albans area, initially forming a second and larger pro-glacial lake in the Watford area (Gibbard, 1977). At least three subsequent glacial advances during this period (Sumbler, 1996) eventually caused the lake to overspill and as a result the southward diversion of the Thames (Gibbard, 1977).

The evolution of the surface and subsurface drainage during this period was extensive. The Proto-Thames had become dammed south east of St Albans and surface water drainage along its axis was largely absent. Gibbard (1977) suggests

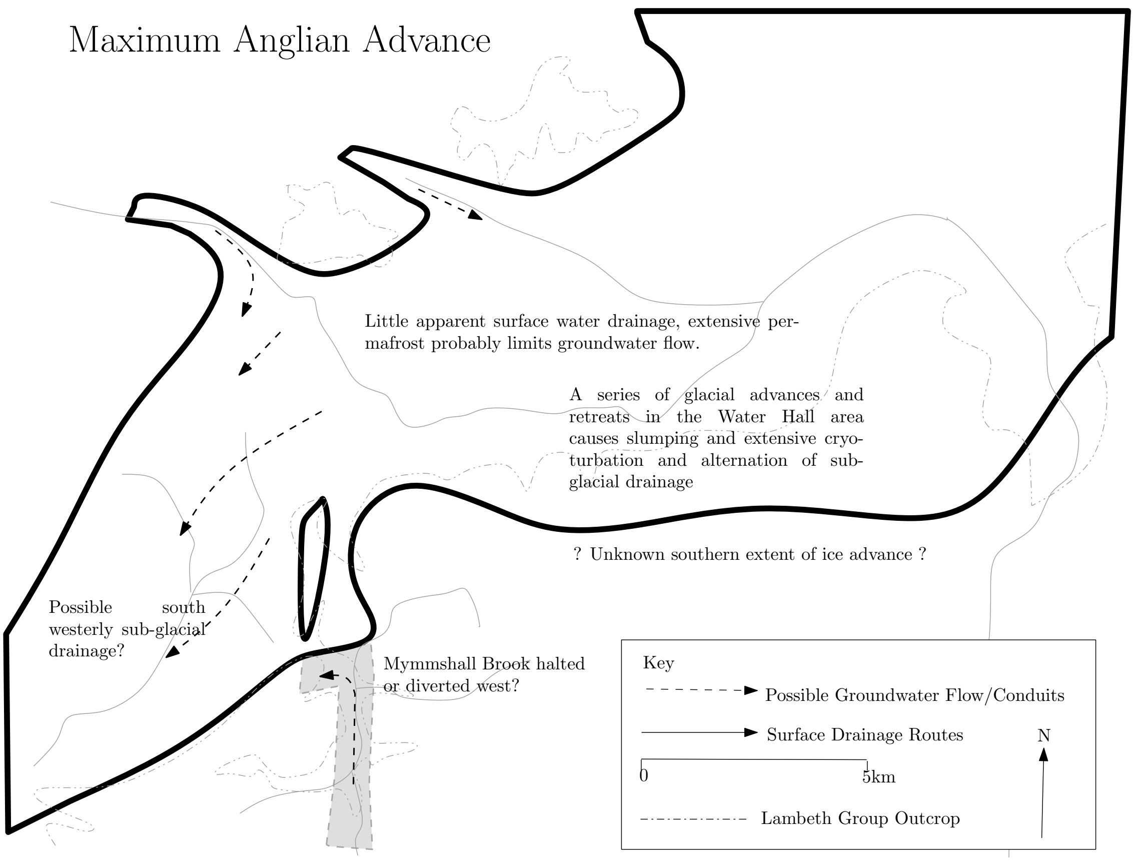


Figure 6.17: The maximum Anglian ice advance (bold line). Surface drainage appears to be limited. The extent of groundwater flow is uncertain and probably controlled by extensive permafrost development. The tributaries that would later become the Mymmshall Brook, Lee and Mimram are all dammed by ice during this period. The distribution of ice, surface drainage roots (excluding that of the Mymmshall Brook) are from Gibbard (1977); Bridgland and Gibbard (1997)

that at least for a time the Proto-Thames may have continued eastward adjacent to or beneath the ice margin and is responsible for the erosion of the embayment of the Palaeocene boundary between Water Hall and Hertford. This course if it occurred (and there is only weak evidence) is nearly coincident with the Palaeocene boundary and the main area of present day solution feature development and it is possible that drainage parallel conduits along this boundary may have developed at this time. McGregor and Green (1978) have also inferred from the distribution of till types and gravels that marginal and sub-glacial drainage may have occurred in an north easterly direction during this period.

Till deposits developed on the Palaeocene escarpment attest that the ice must later have advanced further south (Figure 6.17), although several minor retreats, subsidence and collapse events, possibly associated with surface drainage and development of a localised marginal or sub-glacial lake in the area of Water Hall are described by Gibbard (1977) and might be important in the formation, or weathering of subsurface karst in the area between Water Hall and the Lee Valley.

The cold glacial and peri-glacial conditions, the movement of large volumes of water and the presence of permafrost to constrain flow horizons might also have enhanced the potential for subsurface dissolution along the axis of the Vale of St Albans during this period. The permafrost would probably limit groundwater flow in the interfluves (Younger, 1989) but beneath river channels and perhaps the sub-glacial drainage conditions may still have been favourable for extensive dissolution.

The resulting direction of likely groundwater flow is uncertain, it may have still followed the course of the Proto-Thames to the North-east, or could have followed that of the ice meltwater to the glacial lake in the south east however in either case the probable pre-existing anisotropy developed along the axis of the Vale could be further exploited. Conversely, freeze-thaw weathering and solifluction of the near surface soils and Chalk bedrock and are evidenced by head deposits north west of the Vale of St Albans. This process would probably have disrupted and weathered near surface karst features especially those developed on sloped ground.

As the ice halted an eastward draining river is thought to have developed Gibbard (1977) and might be related to the valley in which the Howe Dell swallow holes are located known as the "Hatfield Meander" and may have exploited the inferred faults and pre-existing topography in this area and could possibly be linked with the evolution of the Mymmshall Brook.

The presence of Kesgrave catchment sands and gravels overlying the Lambeth Group in the vicinity of Brookmans Park and Welham suggest that the Chalk may not have been exposed in the area of the Mymmshall Brook prior to the Anglian Glaciation.

Walsh and Ockenden (1982) suggest that the solution features of the Castle Lime works, as described by Kirkaldy (1950) may have originated at this time beneath a thinned Palaeocene cover and it is possible other dissolution within the valley may have begun to form during this time. This would fit with the initial age of the Mymmshall Brook speculated by Wooldridge and Kirkaldy (1937) that the Mymmshall Brook originated as a northward draining tributary to the Proto-Thames that eventually became dammed by the Anglian ice advance and was forced westward and south and so accounting for the arcuate form of the drainage.

It is possible then that the Mymmshall Brook could be related to the marginal glacial river speculated by Gibbard (1977) and might well have formed the initial valley of the "Hatfield Meander" as a tributary to the Proto-Thames and subsequently any drainage was deflected westward into the Vale of St Albans and perhaps feeding the Pro-Glacial lake.

Early versions of the Lea and Mimram began as glacial outwash streams into the Vale and were then deflected westward along the northern margin of the ice in the Vale (Gibbard, 1977) and are also thought to have fed the pro-glacial lake although these were eventually also dammed by later ice advances.

6.4.3 Post Anglian

As the climate warmed the glacier began to melt in-situ a south westward draining outwash stream developed along the axis of the Vale (forming what is now the Colne) (Gibbard, 1977) and deposited the Upper Gravel deposits of the Vale of St Albans. From the Wolstonian ($\approx 350,000$M.a.) the Lea and Mimram re-established their south westerly flows into the Vale of St Albans and began incision of the glacial deposits and exposing the Chalk (Gibbard, 1977). Various periods of river aggradation and deposition followed through the Devensian and Ipswichian up to the present as the Rivers established their present course and arrangement of fluvial deposits.

In the post Anglian phase (Figure 6.18) it is likely that the majority of the presently observed swallow holes were established in the post glacial period as the till was removed by solifluction and river action especially on the flanks of the Palaeocene escarpment and the Chalk began to be exposed in the Mymmshall Brook valley. The cold conditions would have been favourable for dissolution as run-off tributaries and streams re-established themselves draining toward the Vale and appear to have exploited structural weaknesses, perhaps enhanced by the extensive peri-glacial weathering.

Walsh and Ockenden (1982) suggest that the Water End swallow hole complex may have originated during this time since they probably post date the valley gravels deposited within the catchment of the Mymmshall Brook which are thought to be of post glacial age.

The erosion of the Lea through the glacial and Proto-Thames deposits at this time could also have exposed pre-existing conduits that might have developed beneath the Proto Thames during the pre Anglian phase and these conduits could be responsible for the occurrence of the karst springs at Arkley Hole, Chadwell, Emma's Well and Lynchmill. The modern drainage arrangement might easily have exploited pre-existing karst features along the Vale of St Albans and adjacent to Palaeocene escarpment since they are nearly coincident in alignment.

6.4.4 Present Arrangement

The present day arrangement of the karst system appears to be closely related to that of the Pre-Anglian drainage system, comprising a N-S aligned main conduit path sub-parallel to that of the original course of the Mymmshall Brook through the Hatfield Meander and then turns WSW-ENW along the Palaeocene escarpment following both the course of the Modern Lee and the Proto-Thames.

The karst system is developed along the boundary between in Geomorphic Zone 1 of Maurice et al. (2006) and for the most part the swallow holes are probably post Anglian in age and is fed by active stream sinks extending from at least the

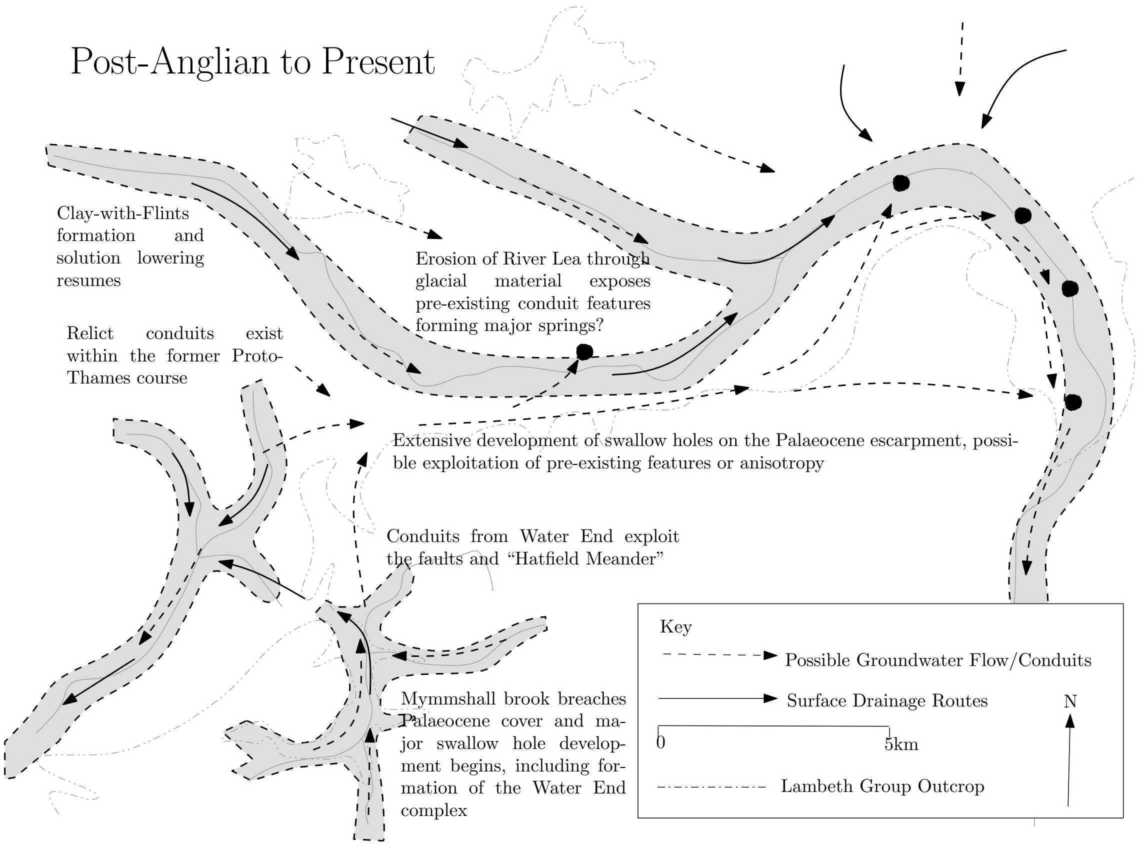


Figure 6.18: Following retreat of the Anglian ice the modern day drainage pattern is established, the Lee and Mimram, originating as glacial outwash streams recapture part of their former flow paths and begin to erode and exploit that of the Proto-Thames. The majority of modern day surface karst was probably initiated during this time. It is possible the major springs might be due to erosion by the Lee exposing relict conduits that have been exploited by the modern day karst system.

catchment of the Mymmshall Brook (Including the Catherine Bourne) and along the Palaeocene Feather Edge to the Lee Valley and also beneath Swallow Holes developed within the Palaeocene outcrop and possibly as far south as the Cuffley Brook.

This system extends into the main axis of the Vale of St Albans and may be exploiting pre-existing relict features or conduits developed sub-parallel to the Proto Thames and it is possible that the main karst springs may represent the Devensian erosion of the Lee to within the Bedrock exposing such features. It is possible that conduits extend elsewhere throughout the Vale of St Albans aligned sub-parallel to the Vale axis or to its tributaries including the Lea, Mimram and their predecessors. The alignment of the possible conduit associated with the groundwater trough between Tyttenhanger and Roestock also closely matches the orientation of the Vale.

Peri-glacial solifluction and freeze-thaw weathering has probably weathered the Chalk surface karst and is mostly likely to have affected the areas peripheral to the glaciation, for example on the Clay-with-Flints capped hills to the northwest of the Vale and could explain the relative sparsity of mapped surface karst in this area.

Table 6.18: Best correlated response times for bromate concentrations to a change in scavenge pumping abstraction at Hatfield PWS (after Fitzpatrick, 2007)

Location	Response time (days)
Hatfield PWS	0
Essendon PWS	2
Turnford PWS	4
Hoddesdon PWS	4
Amwell Hill PWS	5
Broxbourne PWS	5
Amwell Marsh PWS	5
Chadwell Spring	6
Rye Common PWS	7
Middlefield Road PWS	8

6.5 Implications for the Transport of Bromate

The observed spread of tracer occurrence from Water End matches closely the pattern of groundwater sources affected by bromate contamination between Hatfield and Turnford and the inferred travel times show close agreement effects on bromate concentrations at the Lee Valley sources. Between Hatfield and the Lee valley, bromate transport appears to be in large part controlled by groundwater flow in Chalk karst, influenced to a limited extent by abstraction at Hatfield PWS which has been shown to be connected to the karst flow system (Figure 6.19).

6.5.1 Scavenge Pumping at Hatfield PWS and the Karst System

The tracing has provided new insight into how scavenge pumping at Hatfield PWS may be interacting with the karst flow system in order to influence down gradient concentrations. Fitzpatrick (2007) has correlated the lag time between a change in abstraction rate at Hatfield PWS and the observed change in bromate concentration at down gradient locations, in general a 1Ml/day change in abstraction rate results in a $1.5 - 2.5\mu g/l$ change in bromate concentration at Essendon and the Lee Valley wells. Data relating to the peak response times are presented in Table 6.18.

The timing of the peak response is similar to that of the tracer travel times from the Mymmshall Brook catchment. The 2008 tracer test has also established a karstic connection between Hatfield PWS and Water End and along with previous tracer tests, karstic connections between Water End and the major abstractions wells and springs in the Lee Valley. The inferred arrangement of the conduit system connects all three regions along the main route of karst flows. Scavenge pumping at Hatfield PWS influences flows within the karst system via a direct connection which in turn influences the observed concentration of bromate observed at the Lee Valley wells and springs.

This process is likely to be a combined kinematic and solute transport response

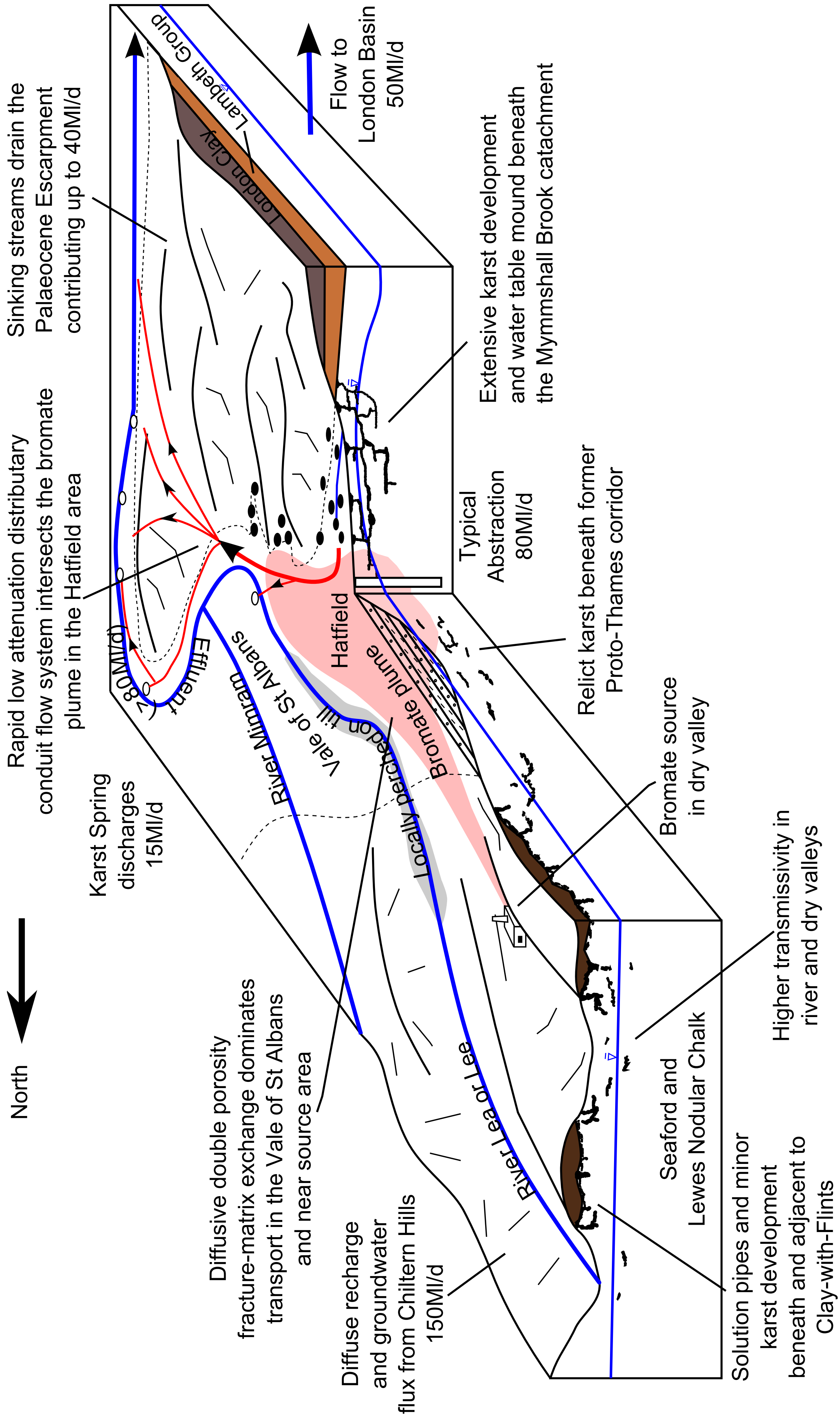


Figure 6.19: Spatial variation of bromate transport towards the Lee Valley

from both the abstraction of water and therefore localised disruption of head and flows within the karst system (possibly close to its entry point) in the vicinity of Hatfield and the through the interception of bromate bearing water and therefore localised reduction of mass in the same area. Since the abstraction at Hatfield PWS appears to have little measurable draw down at observations wells the changes to the local flow regime cannot be easily quantified, however the tracing from Water End does provide a information on the likely solute transport time.

Kinematic response in karst systems, for example due to recharge or abstraction, tends to occur much faster than the equivalent solute transport response and has been observed from a number of analyses of spring hydrographs and chemographs (e.g. Ashton, 1966; Atkinson, 1977; Ford, 2002; Birk et al., 2004) that spring discharge increases first reflect the transmission of the changing pressure wave almost instantaneously through the karst system. Chemical parameters such as turbidity, respond slower reflecting the travel time for the actual physical movement of solutes from swallow holes to springs. The spatial distribution of response times and the travel times of tracer from Water End have been overlaid upon the conduit arrangement in Figure 6.20.

Essendon PWS responds fastest to both abstraction at Hatfield PWS and tracer arrival as might be expected given its closest proximity. Next to respond after four days are Hoddesdon PWS and Turnford PWS, situated in the central southern part of the Lee Valley. Effects are then observed in the northern part of the Lee Valley, including Chadwell Spring and at Broxbourne PWS between Hoddesdon and Turnford. With Rye Common PWS and Middlefield Road PWS respond slowest.

A strong correlation between bromate concentrations at Essendon PWS and Hoddesdon PWS has been demonstrated by (Robinson and Buckle, 2004) during the period at which Hatfield PWS abstractions were negligible. The tracer tests have also indicated there are probably distinct major karst flow pathways to the Hoddesdon/Lynchmill Spring area and the Chadwell Spring area. The spatial pattern of response could therefore reflect the progression of the kinematic wave or perhaps causing a partial de-watering of minor conduits and flow paths which diverge from the main transport routes. The main transport routes respond fastest whilst the minor flow paths, which could be less strongly affected, respond more slowly.

The possible by-pass of Hatfield PWS by the $\Phi X174$ and $MS2$ tracers suggests that the influence of Hatfield PWS does not extend that far to the north and that bromate is entering the main karst flow system in the vicinity of Hatfield, perhaps to the north and east of the Comet Way Borehole.

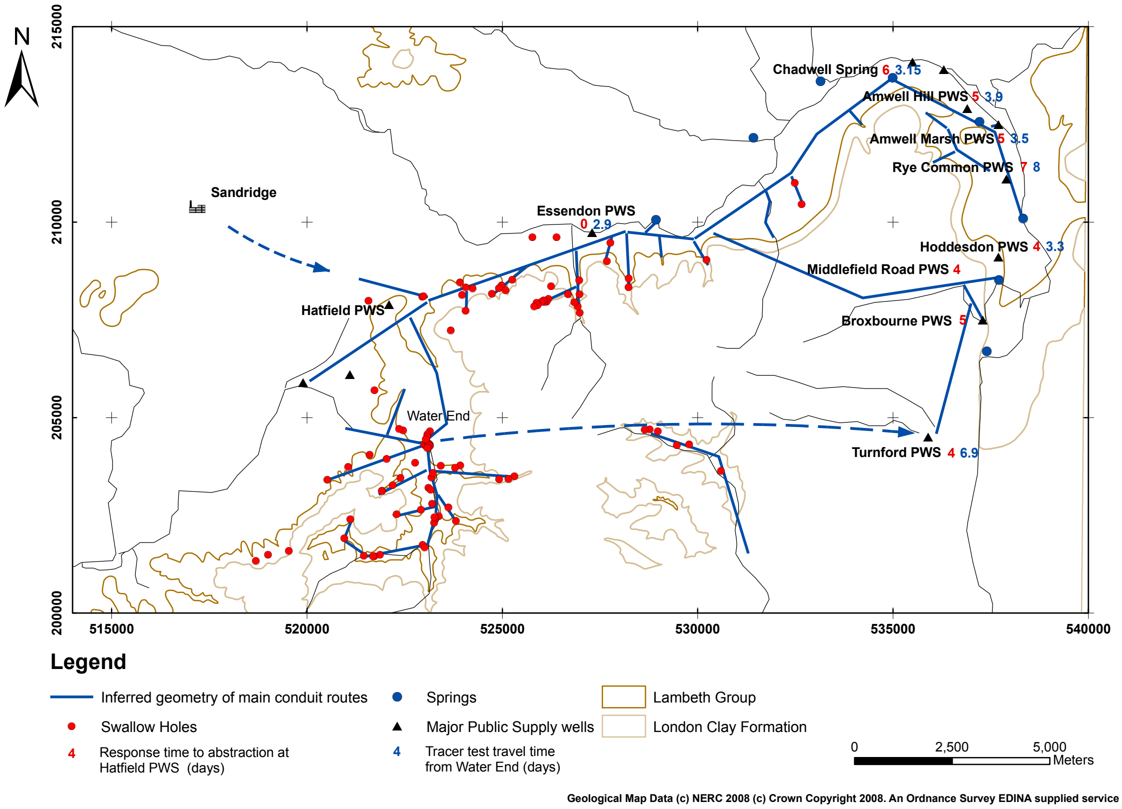


Figure 6.20: Spatial distribution of the response to scavenge pumping at Hatfield PWS, numbers indicate the best correlated response time in days after a change in abstraction rate

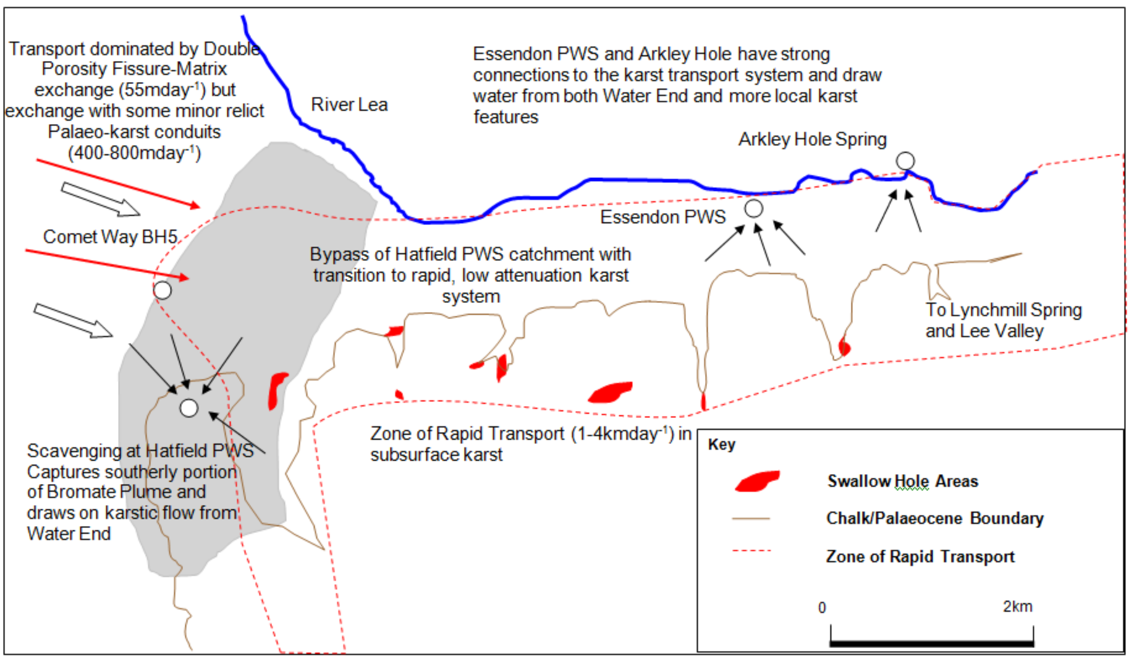


Figure 6.21: Mechanisms of karst flow in the vicinity of Hatfield

6.5.2 Karst and Bromate Transport Within the Vale of St Albans

Surface karst appears is generally absent within the Vale of St Albans probably as a result of extensive glacial deposits covering the Chalk and additional re-working of the Chalk during the Proto-Thames and glacial eras and the subsequent low permeability cap provided by the Lowestoft till which has probably restricted direct recharge across much of the Vale.

However, the 2008 tracer test has provided some evidence that rapid flow pathways extend west from Hatfield across the Vale of St Albans and that such pathways must intersect with the bromate bearing water in the Vale (since both injection locations were positioned close to the bromate "plume" centre) and occurrence at Essendon, Arkley Hole and Lynchmill Spring suggests they directly feed into the main karst system. The flow paths also show evidence of by-passing the scavenge pumping abstraction at Hatfield PWS and thus limit the extent to which the scavenge pumping at Hatfield PWS can protect down gradient locations and hence scavenge pumping at Hatfield PWS may only be having a partial influence on down gradient concentrations (Figure 6.21. The relatively low recovery of the Water End tracer at Hatfield PWS, given the relatively short distance compared to other locations with higher recoveries suggests the connection to the karst system (or the volume of flow) may be less well developed than elsewhere.

The tracer test data also indicate that karst transport within the Vale is subject to greater dispersion and attenuation than that of the swallow hole injection. The breakthroughs suggest a general decline in velocity and mass recovery with distance from the Palaeocene outcrop suggesting that such features are probably weathered but occurrence of tracer at Arkley Hole and Lynchmill Spring suggests they are still connected to the main flow system but a proportion of this flow has at least been intersected by Essendon PWS and possibly Amwell Marsh PWS. Transport velocities in this system appear to be around $20 - 40\%$ of that of the Feather Edge system but the overall recovery of tracers appears to be similar. With the supply of Acidic run-off now dominantly absorbed by the main system developed along the Palaeocene feather edge system it is unlikey that this system is evolving except perhaps close to discharge sites.

In part this may reflect the tracer injection locations not being directly connected to the conduit system and allowing dilution and dispersion before the karst system is reached. It is also possible that the reduced attenuation may be a feature of the karst system itself since greater attenuation of tracers has been observed elsewhere in the Chalk within geomorphic zone 2 of Maurice et al. (2006) in the area up dip of the main Palaeocene escarpment. This increased attenuation has been attributed to weathering, erosion or infilling of conduits in this zone away from an relatively stable source of aggressive run-off from the Palaeocene.

It is therefore likely that within the Vale of St Albans, whilst some rapid flow pathways exist, they are weathered, perhaps poorly connected and could reflect relict features of Proto-Thames age, and so do not dominate bromate transport as they do east of Hatfield. The observed long term stability of bromate concentrations at locations within the Vale also suggests more diffuse and that changes in concentrations are probably buffered by diffusive exchange of the mobile fracture water with the chalk matrix.

Chapter 7

Development of a Distributed Groundwater Flow and Transport Model, Incorporating Karst

Having presented a new conceptual understanding of the Hertfordshire karst flow system in Chapter 6 hydrodynamic parameters have been identified which are applicable to use in modelling studies. Previous attempts to model the catchment scale migration to the Lee Valley and NNR well field have been compromised by an inadequate understanding and/or representation of the Hertfordshire karst system. This chapter summaries the results of previous modelling studies and outlines development of a suite of new models incorporating representations of the karst flow system.

7.1 Representation of Karst in Numerical Groundwater Flow Models

Successful replication of regional scale groundwater flow and transport within karst aquifers is a major modelling challenge since the model must incorporate parameters to represent the high degree of heterogeneity, anisotropy as well as the exchange between the flow components of the matrix, fracture and conduit systems (White, 2002).

The simplest modelling approach is a lumped parameter or black box approach, whereby the karst aquifer is treated as a either single or a series of equivalent porous media cells (e.g. Barrett and Charbeneau, 1997; Scanlon et al., 2003) ignoring the spatial distribution of flows. The required data is simplified to stress inputs and outputs and can be solved by relatively simple linear differential equations. Such models have successfully been calibrated to simulate hydrographs and chemographs at spring or borehole locations (e.g. Long and Derickson, 1999; Maloszewski et al., 2002; Katz et al., 2004). Whilst lumped parameter models can be relatively simple to apply they are limited in use since they can provide no spatial information on the distribution of flows or transport (Scanlon et al., 2003).

The most commonly used aquifer flow and water resources modelling tool is the MODFLOW (McDonald and Harbaugh, 1988; Harbaugh and McDonald, 1996; Harbaugh et al., 2000) suite of codes. The MODFLOW code is a modular finite difference distributed parameter model allowing representation of three dimensional aquifer conditions and a wide range of boundary conditions including, among others, recharge, wells (Harbaugh and McDonald, 1996) and streams (Prudic, 1989). MODFLOW was originally developed to model Darcian flows in porous granular aquifers such as the extensive glacial sand and gravel aquifers found in the United States. However, the flexibility and accessibility of the code has led to a more widespread adoption of the MODFLOW and it has successfully been used for the modelling of fractured aquifers (e.g. Gburek et al., 1999; Jrgensen et al., 2004) including the Chalk (e.g. Gooddy et al., 2001; Grapes et al., 2006; Serhal et al., 2009).

In order to incorporate karst (and fractured aquifers) within the MODFLOW environment an equivalent porous medium (EPM) approach must be adopted. Rather than represent the conduits and/or fractures as discrete model elements the properties of the system are applied to much larger aquifer cell blocks within which the conduits and fractures are contained and are represented as larger effectively "averaged" or "smeared" (Green et al., 2006) computational elements. This reduces the complexity and data requirements of the model and can normally achieve an adequate representation of the large scale karst and fracture flows under a wide range of conditions (e.g. Larocque et al., 1999; Scanlon et al., 2003).

The modular flexibility of the MODFLOW code allows use of boundary conditions to simulate additional aspects of karst systems, particularly the use of the MODFLOW drain package (Harbaugh and McDonald, 1996) which can be used to represent conduits allowing water to be lost from the diffuse aquifer and into the conduit system. Such an approach was adopted by Quinn et al. (2006) and by Zhang and Lerner (2000) to represent adits (effectively man made conduits) in the Chalk aquifer. Scanlon et al. (2003) used single cells with the drain package to represent springs by assigning a high cell conductance, whilst Angelini and Dragoni (1997) used a constant head boundary to model discharge to a single spring.

Although regional scale heads and flows can be successfully simulated in EPM models of karst aquifers, the approach can not accurately represent processes at the scale of individual conduits, for example turbulent flows and the role of temporary storage and exchange between the conduits and the surrounding matrix and fracture system(Green et al., 2006) and can become inaccurate in unconfined aquifers. EPM models are also limited in their representation of transport processes (Teutsch and Sauter, 1998; Svensson, 2001*a*,*b*) since very low values of effective porosity are required (typically $\leq 5\%$) to simulate karst velocities (Shoemaker et al., 2007) and hence the effects of matrix and fracture flows are often neglected.

Extensions to the EPM model can generate a dual or even triple continuum approach whereby separate flow regimes are modelled to represent the matrix, fracture and conduit flows which are each coupled by an exchange term (Teutsch and Sauter, 1998) and have been shown some promise in modelling contaminant transport on relatively small scales (Liu et al., 2003; Vogel et al., 2007).

A further alternative to the EPM approach is often referred to as the discrete approach. In this method the conduits and/or fractures in which flow occurs are represented by discrete model elements, most commonly through the use of finite element methods (for example FEFLOW (Diersch, 1996)) whereby spatial elements can be modelled and the model mesh can be locally refined around individual features. Although they provide a more accurate representation of the aquifer system models of this type require more information relative to EPM models particularly relating to the spatial distribution and orientation of features and their physical dimensions which for reasons of economy and practicality are often not available. This has largely limited the adoption of such models to theoretical use (e.g. Eisenlohr et al., 1997; Kaufmann and Braun, 2000) although some success has been achieved in the simulation of natural systems (e.g. Qian et al., 2006).

The most recent development in the modelling of karst aquifers is the introduction of coupled dual conductivity models that combine aspects of both equivalent porous media and discrete approaches. A dual conductivity approach couples flow in a diffuse continuum representing the aquifer matrix, typically represented by an equivalent porous media model, with a discrete model of the conduit network via a linear exchange term. A number of dual conductivity packages based upon these principals have been developed, many of which use the MODFLOW package to simulate the diffuse flow component e.g. the Carbonate Aquifer Void Evolution model (CAVE) (Liedl et al., 2003) for MODFLOW-96, dual conductivity package for MODFLOW (MODFLOW-DCM) (Green et al., 2006) and the conduit flow process package for MODFLOW CFP-MODFLOW (Shoemaker et al., 2007) which is itself based upon the CAVE code.

Dual conductivity models present many advantages over discrete and EPM methods by allowing proper physical representation of turbulent flows within conduits, including open channel flows combined with the robust and proven simulation of diffuse flows by MODFLOW. However, the methodology is relatively new and still subject to a number of limitations:

- As with discrete models, the user must infer or have knowledge of the position (both vertically and horizontally) of the location of conduits within the system

- The user must also supply additional parameters to describe the conduit system including diameter of the voids, roughness and tortuosity, Reynolds num-

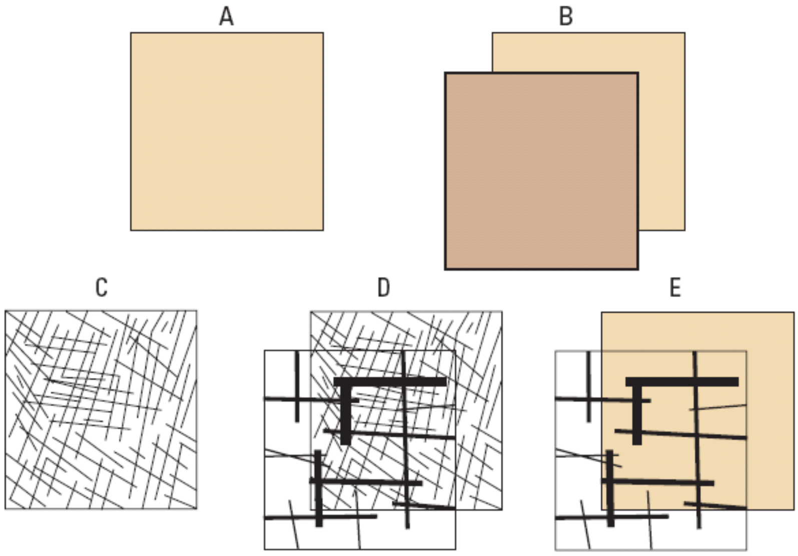


Figure 7.1: Methods for representation of karst flow systems in numerical models (Shoemaker et al., 2007). A=Equivalent porous media, B=Dual porous media model, C=discrete fracture method, D=Two region discrete fracture method, E=Coupled dual conductivity coupled model

bers and an exchange term or conductance to describe the transfer or flows between the diffuse and conduit systems (Green et al., 2006; Shoemaker et al., 2007)

- Both MODFLOW-DCM and CFP-MODFLOW are restricted to single layer models and do not currently include representation of solute transport processes (Green et al., 2006; Shoemaker et al., 2007)

- Although CAVE does allow modelling of solute transport its use is limited to confined aquifer systems (Green et al., 2006)

The methods available for the simulation of flows and transport within karst aquifers are summarised schematically in Figure 7.1, the development of these methods is ongoing and presently all are subject to limitations in their application, particularly in modelling contaminant transport.

Development of an appropriate representation of the Hertfordshire karst system in simulations of bromate transport will be evaluated in the light of these limitations and uncertainties they impose upon model outcomes.

7.1.1 Existing Models of the Bromate Problem

The earliest modelling assessment undertaken with respect to the bromate contamination by was conducted by Chemfix (1984) and (1985) between 1984 and 1985 prior to the redevelopment of the St Leonard's Court site. The models were based on a point source of contamination within a simple two dimensional flow field and suggested that contamination of near source boreholes within the Sandridge area might occur if the site remained undeveloped and open to infiltration. It was also suggested that abstraction locations would be unaffected. The study was simplistic and resulted in an underestimate of the extent of contaminant migration. The method was criticised by (Thomas, 2001) for not considering the Chalk aquifer correctly, particularly with respect to preferential fracture flow as well as in the adequate conceptualisation of the contaminant source and overestimation of infiltration rates.

A series of further analytical models based on the Environment Agency remedial targets methodology was undertaken in 2001 by Thomas (2001). Over 60 different simulations were modelled to represent various possible flow paths from Sandridge to down gradient receptors, principally Hatfield PWS using different possible representations of dispersivity and source concentration. Whilst the analysis yielded a number of insights relating to the likely geometry and flow path of the main bromate "plume" insufficient data was available, particularly for groundwater flow velocities and aquifer properties to develop a robust prediction of future bromate concentrations.

A major modelling study, known as the Bromate Groundwater Flow Model (BGFM) was initiated as a joint project between the Environment Agency and Three Valleys Water and is detailed by (Buckle, 2002, 2003). The approach used the MODFLOW-2000 groundwater flow model (Harbaugh et al., 2000) coupled with the mass transport in three dimensions (MT3D) model (Zheng and Wang, 1999). The BGFM was developed as a single layer model taken as a subset from a regional scale groundwater resource model for the Chiltern Hills, the Upper Lee and Mimram Model (ULMM) developed by Entec (2000).

The flow model inherited a number of problems from the parent regional scale model relating to the balance of water between the Ver and Lee catchment and the direction of groundwater flows within the Vale of St Albans immediately down gradient of Sandridge. The MT3D transport modelling indicated further errors, the deficiencies in modelling flow directions within the Vale of St Albans prevented adequate representation of the plume geometry within the Vale of St Albans leading to modelled breakthrough of bromate at Roestock PWS (where it is not currently observed) and an underestimate of concentrations at Essendon PWS ($\leq 1\mu$g/l). These deficiencies could not be improved by additional calibration and the use of the model was subsequently suspended pending a review of the conceptual understanding (Buckle, 2003).

The analytical dual porosity transport code DP-1D (Barker, 2005) (see section 6.2) was employed by Robinson and Buckle (2004) to determine bromate concentrations for three flow pathways: 1) Orchard Garage (a monitoring location just east of Sandridge) to Hatfield PWS, 2) Orchard Garage to Essendon PWS and 3) from Hatfield PWS to Hoddesdon. For each case a constant concentration source was adopted between 1965 and 2000 (1000μg/l at Orchard garage and 200μg/l at

Hatfield PWS) for 2000-2004, the time series of observed concentration data at the modelled source locations. Subsequent to 2004, a constant concentration was again adopted; 1000μg/l at Orchard Garage and 244μg/l at Hatfield PWS. Aquifer parameters were derived from literature data in the absence of site specific data relating to Hertfordshire and are consistent with that for the UK Chalk aquifer as outlined in Chapter 3. The DP-1D simulations were able to achieve the same order of magnitude representation of concentration trends at Hatfield and Essendon, including the observed long term rise in concentration, but did not replicate seasonal behaviour due to the non seasonality of the 1 dimensional model, the constant source and the smoothing effect of the dual porosity diffusive exchange. The rising trend was interpreted as suggesting that fracture and matrix concentrations had not yet reached equilibrium at Hatfield PWS or Essendon PWS (Robinson and Buckle, 2004).

A catchment scale flow and transport model using MODFLOW and MT3D-MS, known as the Northern New River model (NNRM) was also developed by Assem (2005) and Buckle (2005) to attempt to model transport of bromate to the Lee Valley. The model was developed by merging the Upper Lee and Mimram resources model of Entec (2000) and then extended south and east to include the Lee Valley. The model was developed in a transient state replicating observed flow conditions from 1965-2004 and from 2004 to 2029 using a repeat of the 1979-2004 boundary conditions to provide long term predictions of bromate concentrations. Calibration of flow and transport of bromate was improved relative to the previous BGFM and the relative spatial distributions of groundwater levels better reflected that of observed data, however a number of deficiencies remained:

- Observation Boreholes in the Upper Lea, Ver and Mimram catchments all show a slight lag in the timing of water level maxima and minima and almost all calibration boreholes, particularly those in the Vale of St Albans and Upper Lea indicate much lower water level minima than observed in drought years, notably the period 1991/92 and 1997/98 and this applies to both the BGFM and the NNRM.

- Water level calibration at Orchard Garage and Hatfield Quarry, close to the Bromate source is relatively poor. At Orchard garage water levels are overestimated whilst at Hatfield quarry they are generally underestimated. This is likely to result in an overestimate of hydraulic gradient in this area and therefore a differing flow regime to that observed.

- Groundwater levels at Essendon are systematically over-predicted by approximately 5m and levels at Chelsea Cottage (approximately in the centre of the NNR field) are under-predicted by the NNR model by approximately 5-8m. The NNRM also indicates a much more variable range of water levels with greater amplitude between maxima and minima than are observed for calibra-

Table 7.1: Range of aquifer parameters adopted in the NNRM of Buckle (2005)

Parameter	Range
Hydraulic Conductivity	1-150m/day
Storage Coefficient	0.03-0.1
Matrix Porosity	0.38%
Effective Porosity	$1 - 5\%$
Dispersivity	200m
Mass Transfer Coefficient	1×10^{-5}

tion boreholes in the Middle Lee area.

- Modelled water levels in the vicinity of the North Mymms recharge mound are slightly over-predicted (in October 2000) and the spatial extent of the mound is larger than observed.

Transport in the model used the multiple species version of MT3D (MT3D-MS) which is capable of simulating dual porosity exchange through a first order exchange (see Section 6.2). As with previous models, a constant source of bromate was modelled, in this case of 5000μg/l at the location of St Leonard's Court Sandridge. The shape and magnitude of the apparent "bromate plume" (Figure 7.2) is well replicated by the model between Sandridge and Essendon PWS but the model underestimates the further migration of bromate to the NNR well field.

Table 7.1 indicates the range of aquifer parameters adopted in the NNRM. Generally these are consistent with those established for the Chalk aquifer in Chapter 3. Attempts to improve model calibration by varying the mass transfer coefficient, dispersivity and effective porosity and source concentration were able to increase migration toward the NNR well field, however this was at the expense either of model stability or of the modelled plume geometry resulting in a much wider bromate plume than observed.

7.1.2 Karst Representation in the Northern New River (NNR) Model

The previous modelling exercises have been unable to replicate the full range of observed aquifer conditions, and in particular, have not be able to simulate the migration of bromate to the NNR wells via the Hertfordshire karst system. The role of the karst in the transport of bromate was acknowledged in the conceptual understanding underpinning the NNRM (Buckle, 2002) however the representation of the karst system within the model is limited. In part this was due to deficiencies in the conceptual model and inadequate data to properly parameterise the system at that time.

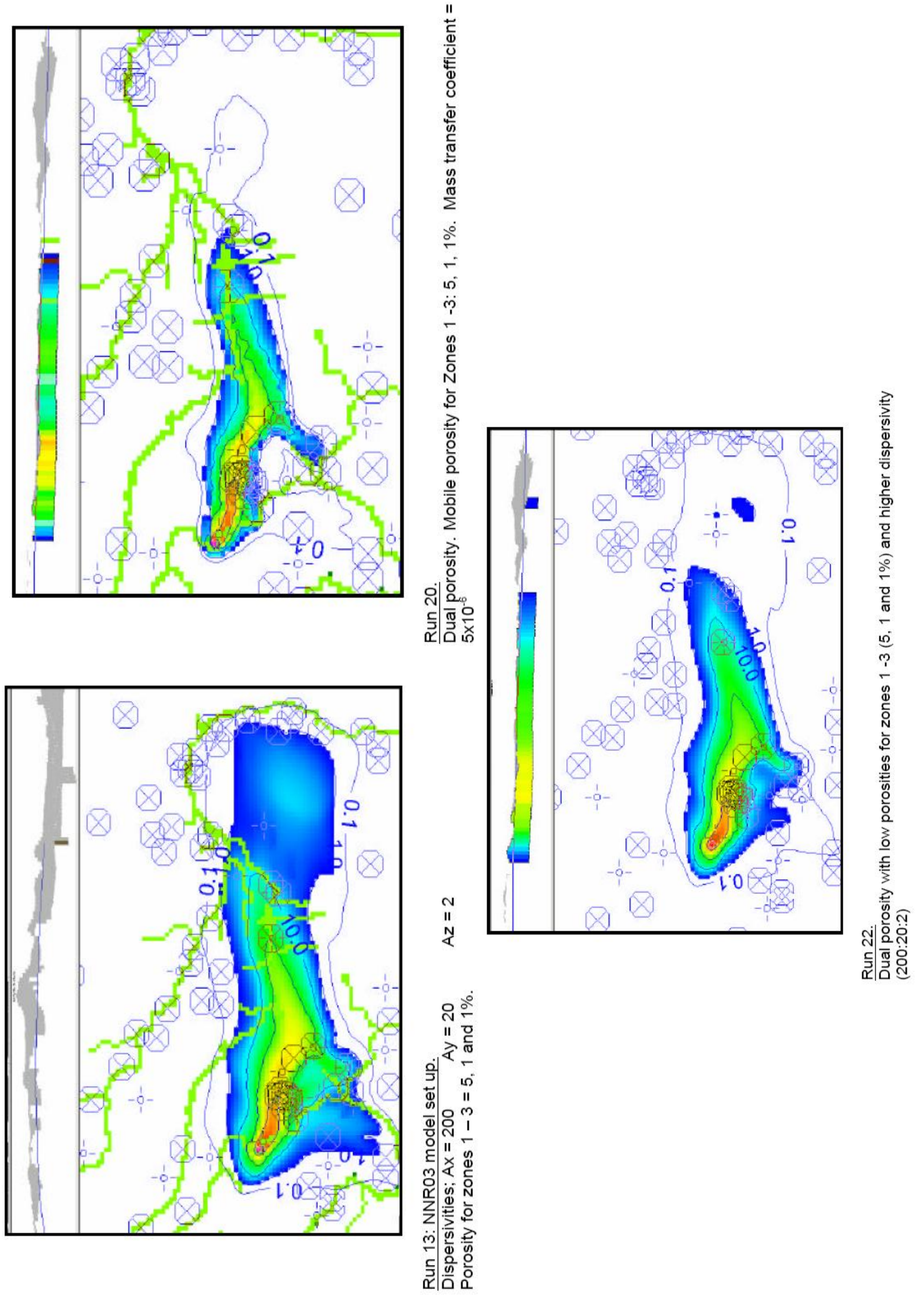


Figure 7.2: Representations of bromate transport using the NNRM (Buckle, 2005)

Table 7.2: Summary of the recharge zones adopted in the 4R Model (Buckle, 2002)

Recharge Area	Geology	Recharge Model
Overlying Formations	Clay-with-Flints and London Clay	No recharge permitted, Mains leakage added to surface run-off
Urban (Chalk)	Chalk underlying urban areas	10% SMD bypass up to maximum of 50mm/day. 30 day lag of recharge. Slow release of run-off and mains leakage
Urban (Till)	Urban areas underlain by Lowestoft Till	Maximum infiltration of 1.5mm/day, any excess released to surface run-off. Slow release of run-off and mains leakage
Rural (Till)	Rural areas underlain by Lowestoft Till	Maximum infiltration of 1.5mm/day, excess is released to run-off
Rural (Chalk and permeable drift)	Rural areas underlain by Chalk, Reading formation and gravels	10% SMD bypass to maximum infiltration of 50mm/day with 30 day lag of recharge
Swallow Holes	Chalk	10% SMD bypass to maximum infiltration of 100mm/day with 30 day lag of recharge

7.1.2.1 Boundary Conditions

The principal representation of karst in the NNRM is within the recharge and stream flow boundary conditions. The NNRM is transient and uses monthly stress periods with each boundary stress being applied as a average daily rate for that month.

The recharge boundary conditions have themselves been defined by a separate stand alone model, the Rainfall Runoff Routing Recharge model (4R) developed in house by Entec Ltd (Entec, 2001). The 4R model is based upon a daily time step soil moisture balance with sub-packages to represent urban leakage (based upon population density) and geological variation. The output of the model is a daily time step recharge stress which is averaged by month to provide direct input to the MODFLOW recharge package. Under this methodology the model area is sub-divided into recharge zones based upon the land use and soil/rock type, this generated recharge and runoff and distributions in a format suitable for input to MODFLOW. The same methodology has been applied through the ULMM, BGFM and NNRM with minor modifications to either update input data (e.g. rainfall records) or by changing the model extent.

Swallow holes were represented in the recharge model by allowing a 10% soil moisture deficit (SMD) bypass up to a maximum recharge of 100mm/day, with a 30 day lag also applied. The spatial distribution of the 4R input data and recharge zones was not reported however, a summary of long term daily average recharge for the modelling period from 1965-2004 is presented in Figure 7.3.

Figure 7.3 illustrates recharge being greatest in the north and west of the model region, decreasing to the east and south with the London Clay forming a large area with negligible recharge. High recharge is also associated with the edge of impermeable deposits and urban areas to simulate mains leakage and run-off. Localised

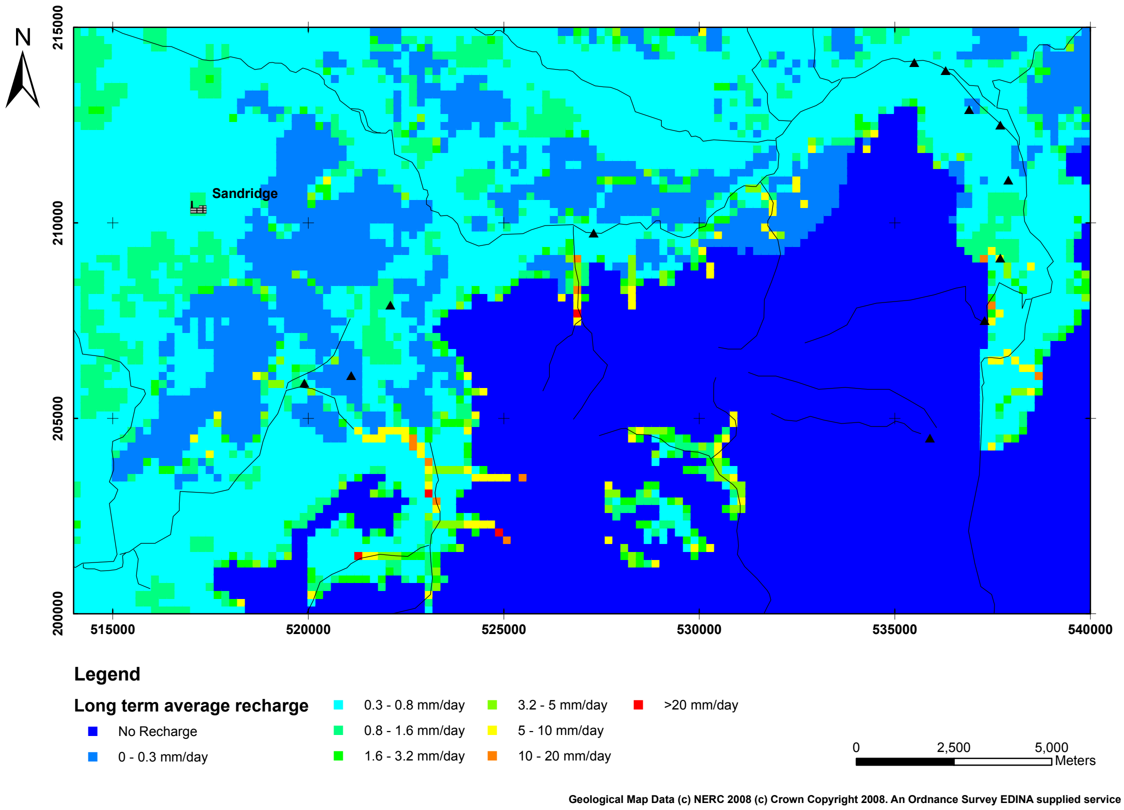


Figure 7.3: Average recharge (1965-2004) input data for the NNR Model in mm/day. Locations of major rivers and streams are shown in black.

"hot spots", usually comprising single model cells occur at the position of swallow holes and also is concentrated along river and stream valleys. The contribution of run-off for the Mymmshall brook that originates on relatively impermeable London Clay south of the Model extent is included as additional run-off recharge added to this area.

It is uncertain to what extent SMD may influence flow through the swallow holes, the majority of flow probably enters directly into solution cavities from the streams and may have very little contact with infilling deposits. If the infill is dominantly loose sand, as appears from Walsh and Ockenden (1982), reduced capillary tension in these deposits may result in reduceded sensitivity to SMD and a greater proportion of bypass flow than that currently allocated (which is the same in the 4R model as for other Chalk areas).

Justification for the introduction of a lag time for recharge, and a description of the exact mechanism by which it is applied for the swallow hole cells is not provided in (Buckle, 2002), bet generally a lag time does not fit with the conceptual understanding. The lag may represent delayed run-off from the Mymmshall Brook catchment which extends beyond the model boundary, although flow the Mymmshall Brook appears to respond relatively rapidly to rainfall events (Atkins, 2006). Neither the SMD bypass nor the introduction of a time lag may be justified on a physical basis and it is possible that recharge via swallow hole cells is underestimated by 4R.

Rivers and streams within the modelled catchments are represented using the stream flow (STR) MODFLOW package (Prudic, 1989). Stream locations are shown in Figure 7.3, allocated to the valleys of Gade, Ver, Lee, Mimram and Colne. Some cells are also added to tributary valleys including parts of the Mymmshall Brook and the Sandridge dry valley to represent potential ephemeral flows and allow surface water infiltration to simulate swallow holes. Stream cells were specified within the active aquifer layer. A single stream bed thickness of 0.1m was uniformly applied to all stream cells; the stream bed conductance was varied generally between 200 − 1600m^2/day. The lower reaches of the Mym

Stream bed conductance in the Mymmshall Brook and swallow hole stream cells and some of it's tributary valleys (e.g. the Catherine Bourne) has been set to 10000m^2/d, this is broadly consistent with that for a well sorted sand or gravel and hence is probably a good representation of foundered Reading Formation sands in dissolution features or reworked Reading Formation in stream bed sediments.

Separate calibration of the NNRM against flows for the ULMM, BGFM and stream flow gauging. Specific data are not provided but descriptive information indicated that groundwater inputs and stream flows closely match those in the BGFM and gauged flows although inputs into the Colne are slightly lower (Buckle, 2005). This might in part be due to overall under-prediction of heads in the Lower Colne valley or could be indicative of a deficiency in the recharge model. Calibration data for surface waters provided for the BGFM indicate the following:

- Under-prediction of flow in the River Ver at Hansteads
- General over prediction of flow at Luton Hoo
- Over-prediction of flow at Water Hall

One major omission in respect of karst in the NNRM boundary conditions is that of spring discharges; the karst springs form important natural discharge points however none have been directly incorporated within the model. Although the stream flow boundary cells do allow water to leave the model based upon relative heads and conductance they do not always intersect with the locations of springs. In particular Arkley Hole, Chadwell Spring and Lynchmill Spring are all located off the main course of the River Lee. Calibration data for flows both in and out of the karst system are not provided for any of the models and it appears that calibration of this behaviour has not been undertaken. As a result it is difficult to infer how closely (if at all) the karstic behaviour of the region is represented in the flow models.

7.1.2.2 Aquifer Parameters

In the development of the NNRM a revision of the aquifer parameters was undertaken to improve representation of the karstic zone compared to the BGFM. The results of the calibration of hydraulic conductivity are shown in Figure 7.4. Hydraulic Conductivity values were increased to 50m/day in a narrow zone extended between the between North Mymms swallow holes and Arkley hole then extending eastward towards Lee and the NNR wells. Although relatively high, a 50m/day zone is not significantly greater than the conductivity used in other areas of the model to represent the high transmissivity of Lee valley. During calibration a further high conductivity zone (150m/day) was added between Essendon and Hoddesdon based partly on an observed improvement in model performance and the results of historical tracer testing of Harold (1937).

Figure 7.4 illustrates how the calibration of the geometry of the high hydraulic conductivity zone focused on replicating the apparent distribution of the bromate occurrence rather than representing the actual distribution of karst features in a physically realistic way. The zone of swallow holes developed within the grounds of Hatfield Park immediately east of Hatfield lies outside the derived karst geometry of the NNRM. Much of the Mymmshall brook catchment is also assigned a low hydraulic conductivity ($\leq$ 3m/day). A similar approach was taken in the parameterisation of effective porosity.

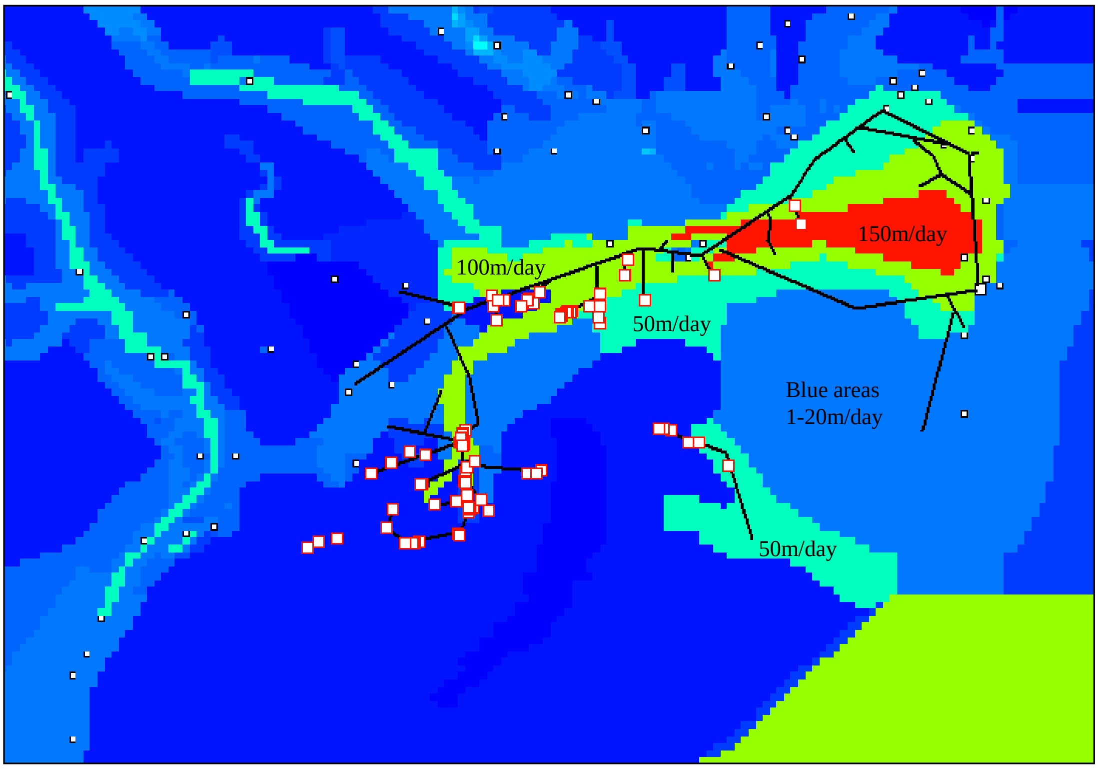
That the karst system is not represented in the NNRM in a realistic way is illustrated by a simple calculation of advection velocities within the model. Assuming the adopted hydraulic conductivity values for the karst zone of 150m/day and effective porosity of 0.5% (Assem, 2005) and a typical hydraulic gradient for the zone of 0.003 would give equivalent flow velocities of 90m/day, much slower than that observed for the karst system and it is unsurprising that migration of bromate to the NNR wells is a major deficiency in the model. Attempts to increase flow velocities by further reducing effective porosity but could not be achieved owing to model instability (Buckle, 2005).

7.2 Development of New Models for Bromate Transport

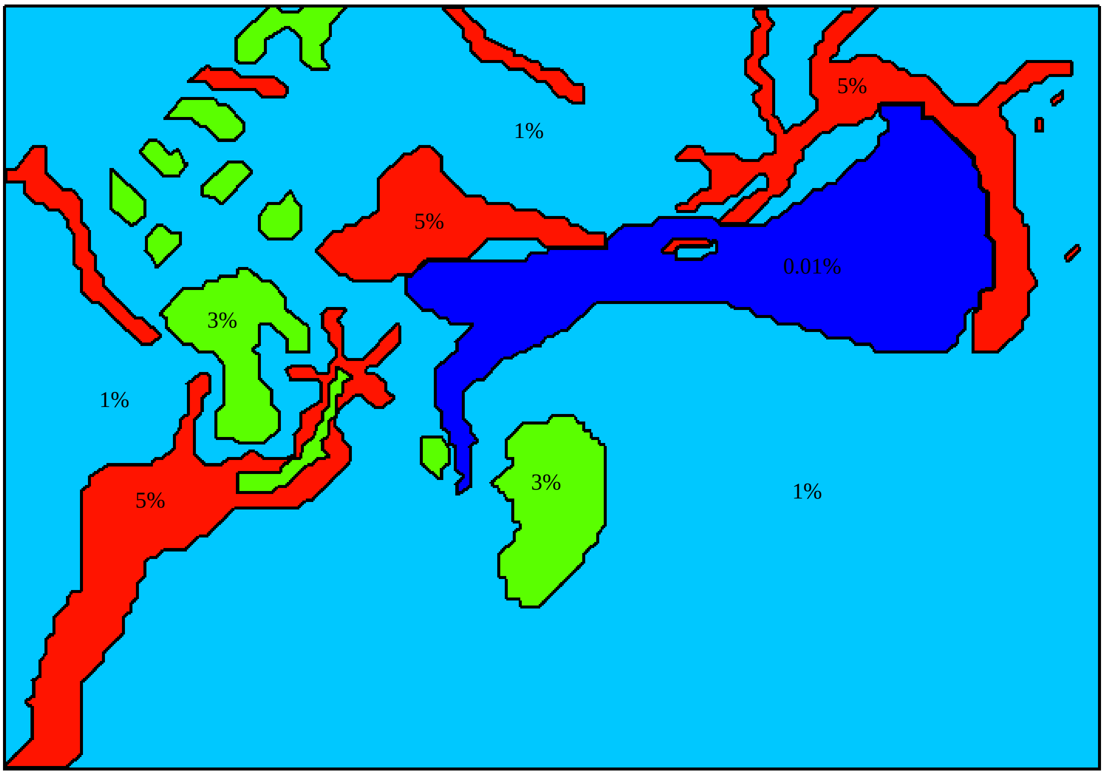
7.2.1 Modelling Strategy

Having established the methods available for simulating regional flow and transport in karstic aquifers, and the apparent deficiencies in the representation of karst within existing transport models of bromate in Hertfordshire, there is a clear requirement for the development of new groundwater flow and transport models. A better representation of the new conceptual understanding of the Hertfordshire karst should improve a major shortcoming within current models, that of bromate transport to the Lee Valley and NNR well-field. Within this overall strategy a number of target criteria are defined:

- Simulation of aquifer heads and flows should provide a similar or better statistical fit to observed data as previous groundwater models (e.g. the ULMM,



(a) Hydraulic conductivity distribution



(b) Effective porosity distribution

Figure 7.4: Distribution of hydraulic conductivity and effective porosity in the NNR Model of (Assem, 2005). Swallow hole locations are shown as white squares and the inferred conduit geometry as black lines. Representation of the karst geometry appears to have been undertaken on basis of replicating the bromate plume rather than the physical reality of the karst features of the aquifer.

BGFM or NNRM).

- The spatial distribution of aquifer parameters should be directly derived from the conceptual understanding as outlined in Chapter 6.
- A new model should be able to replicate the connectivity and travel times demonstrated by the bacteriophage and 20th century tracer tests on a catchment scale.
- Spring locations and flows should be incorporated into the model both as a physical process and as criterion for calibration.
- Observed bromate concentrations should be used as calibration and/or validation data.
- Distributed modelling should allow development of representative flow pathways, calibrated against tracer and bromate connectivities for use in a "Multiple Analytical Pathways" modelling approach by Fitzpatrick (2010). This approach can simulate both dual porosity diffusive and karst conduit transport along flow paths from source to key receptors in the Hertfordshire catchment.

Fulfillment of these criteria should ensure that both the conceptual understanding and observed data are adequately represented by the model, thus increasing confidence in model output.

Since contaminant transport modelling of the bromate contamination forms a core element of model development, this prevents the use of the dual conductivity pipe flow models (e.g. DCM-MODFLOW, CFP-MODFLOW) since they are not compatible with the transport packages for MODFLOW in their present form. Although the distribution of conduits has been inferred, it is poorly constrained, particularly in the vertical dimension and conduit sizes can only be estimated. The use of a pipe flow model would increase the uncertainty in parameter estimates and reduce confidence in the calibration of the model. Insufficient data regarding fracture and conduit geometries also limits effective implementation of a full discrete model of the aquifer using finite element methods.

Since more complex models are not practicable for the modelling of bromate within the Hertfordshire karst system an EPM model will be adopted. The data requirements for such a model are consistent with those already available and are compatible with the existing suite of flow models which have already achieved a reasonable calibration for heads and flows in the Hertfordshire Chalk. Existing recharge and stream flow models already incorporate a basic representation of karst. A further advantage of adopting an EPM is that if at some future date dual conductivity pipe flow models are developed to allow proper representation of solute transport the EPM could be converted to a pipe flow model by addition of the discrete pipe geometry into the model.

EPM models of transport processes in karst systems are limited (Scanlon et al., 2003; Green et al., 2006; Shoemaker et al., 2007) because of the assumption of low effective porosity and storativity required to force rapid changes in concentration and movement of flows is not representative of the actual state of the aquifer. In addition karst transport occurs within discrete highly heterogeneous flow networks not easily represented by a porous medium. In the Chalk aquifer, both effective porosity ($\leq$ and storativity (0.0004-0.004 (MacDonald and Allen, 2001)) have been shown to be low (Watson, 2004), since nearly all effective flow and storage on short time scales is as a result of the fracture and or conduit system (see chapter 3) and hence the disparity in an EPM model of the karstic Chalk may be less significant than for other aquifers.

The distribution of karst in Hertfordshire is rather localised to the Palaeocene feather edge, although some elements may extend into the Vale of the St Albans, however on a broad scale the heads and flows within the aquifer have been adequately represented by a EPM model (Entec, 2000; Buckle, 2003, e.g.).

A further advantage of adopting an EPM approach, especially in the MODFLOW environment, is that it allows use of multiple representations and methods for solute transport modelling, either through the use of the in-built packages or the additional MT3D-MS package (Zheng and Wang, 1999) both of which allow the use of a dual domain (mobile and immobile water elements) option for simulation of solute transport via first order exchange between the two. Additionally the use of the MODPATH package to simulate advective transport allows simulation of aquifer connections to ensure flow directions are appropriate and representative for the Hertfordshire karst. Flow paths calibrated by this method can also be used to derive "multiple analytical pathway" models to properly simulate diffusive and karst conduit transport (Fitzpatrick, 2010).

However, there remain shortcomings in the representation of karst flow systems using EPM models. By adopting an EPM model for the Hertfordshire karst system an assumption is made that within those cells designated with effective properties of the karst system, representation of flows and transport within that system relates solely to the conduit system and the contribution of fractures and matrix (the dual porosity Chalk) is not represented. This assumption is reasonable since the tracer tests have demonstrated that within the karst system transport is dominated by the conduits with rapid flow, low attenuation and relatively little tailing due to exchange with immobile groundwater.

7.2.2 Replication of the NNRM

To maximise compatibility with existing models initial modelling work was undertaken in MODFLOW-2000 (Harbaugh et al., 2000) within the Argus Open Numerical Environment (ONE) version 4.2.0w (Argus, 1997) using the MODFLOW

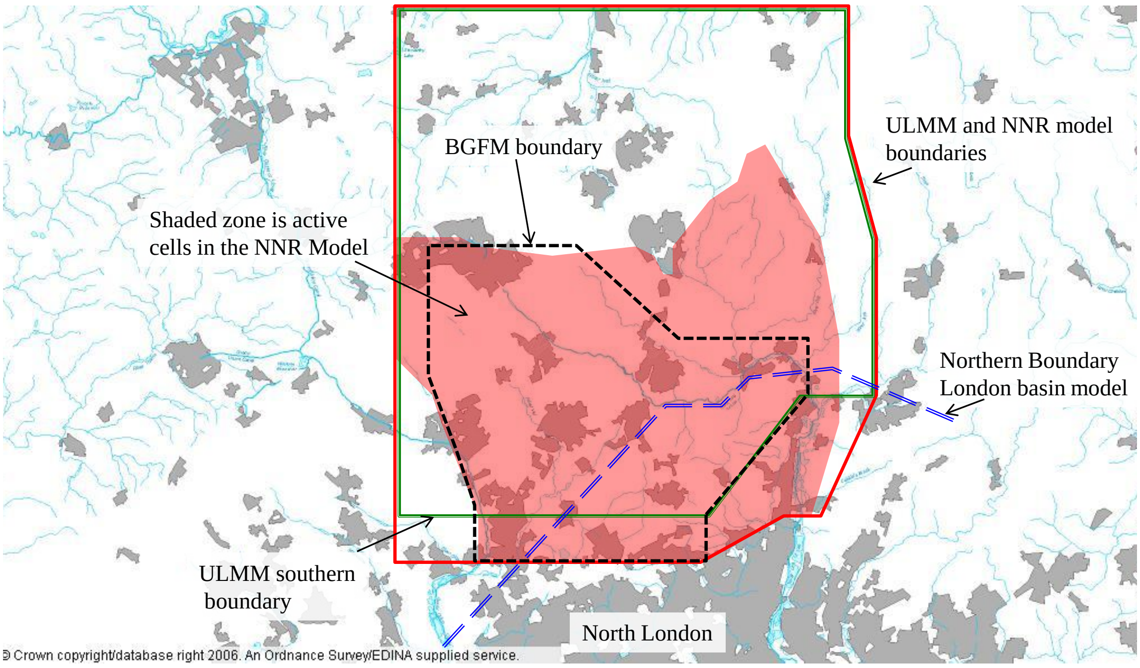


Figure 7.5: Spatial distribution of the NNR groundwater flow model and its parent models showing the external boundary conditions.

graphical user interface (GUI) version 4.31 (Shapiro et al., 1997; Hornberger and Konikow, 1998; Winston, 1999, 2000) developed by the U.S. Geological survey. The NNRM was originally developed within the Groundwater Vistas GUI and so was not directly compatible with the MODFLOW-GUI for Argus ONE. The NNR input files in MODFLOW formats were provided by Atkins Global Limited. The initial modelling stage was to replicate the NNRM within Argus ONE.

7.2.2.1 NNR Model Discretisation and Boundary Conditions

The NNRM is a transient model with 477 monthly stress periods covering the period January 1965 - September 2004, each stress period having three time steps with aquifer stresses applied as daily rates averaged over the stress period.

The model is constructed from a two layer finite difference grid of 250 x 250 square cells with each cell being 200m in width. The spatial extent of the grid covers the area between NGR 500000 195000 in the south west corner and NGR 550000 245000 in the north east and is presented in Figure 7.5. The figure indicates that the boundaries of the NNRM are approximately coincident with the parent ULMM although the NNRM has been extended south and east to include the lower part of the River Lee. A large proportion of the NNRM has been designated as no flow and much of the shared boundary with the ULMM has no defined boundary condition and the "external" boundary conditions are actually wholly within the spatial extent of model domain except along the southernmost boundary. The flowing area of the NNRM therefore bears more similarity to that of the BGFM although it has been extended and boundaries revised.

No-flow boundaries have been applied to the western, northern and eastern model boundaries which are considered to represent regional groundwater divides or flow lines (Buckle, 2005). No temporal variation has been assigned to the no flow boundaries. All of the numerical models of relevance (the ULMM, BGFM and NNRM) have been comprised of two model layers. The elevation of the upper surface of the top layer has been defined to model the regional topography. No groundwater flow occurs in this layer and it has been defined as inactive although the defined topography does influence the 4R recharge model as described in section 7.1.2.1.

The southern boundary has been assigned using the general head boundary package to simulate flux out of the catchment into the London Basin (Buckle, 2005). The general head flux boundary was calibrated using volumetric flow data obtained from approximately coincident cells within the London Basin Groundwater Flow Model of Mott MacDonald (2000). The NNRM typically underestimates the modelled flows to the London Basin as determined by the LBGFM. In the extreme southwest of the model, calibration indicates flow into the model from the London Basin. This might relate to draw-down due to abstractions at Bushey PWS close to the model boundary.

The lower active flow layer comprises an EPM representing the Chalk and the other minor aquifer units (such as the Lower Glacial Gravels). All these units are treated as a single layer with a single hydraulic conductivity for the total depth. The geometry of this layer was defined by Entec Ltd during development of the ULMM (Entec, 2000) with upper surface of this layer being derived from the top of the Chalk and sand and gravel units in hydraulic continuity where present (e.g. the Kesgrave Gravels and Reading Formation).

The lower boundary represents the base of the effective aquifer and is defined as a no flow boundary 60m below the initial head of each cell. Locally, close to groundwater abstractions points, cell thicknesses were extended to improve model convergence. Where confined conditions were apparent the lower boundary was taken to be 60m below the base of the confining layer (Buckle, 2005).

Overall this may underestimate the effective aquifer thickness in places as indicated by a number of wells (e.g. Hoddesdon PWS) that extend to depths greater than 60m below the rest water level in the Chalk. The aquifer thickness as defined excludes the possibility of representing discrete preferential flow horizons at greater depths. For example, contributory flow is inferred in places from deep fractured horizons such as the Chalk Rock or Melbourn Rock (See Chapter 3).

The major surface water systems are represented in the MODFLOW model by stream cells. In the BGFM these comprised 1509 discrete stream cells transferred from the ULMM as illustrated in Figure 7.6. Additional stream cells were added to dry valleys (Assem, 2005) including parts of the Mymmshall Brook, to represent potential ephemeral flows. A single stream bed thickness of 0.1m was uniformly

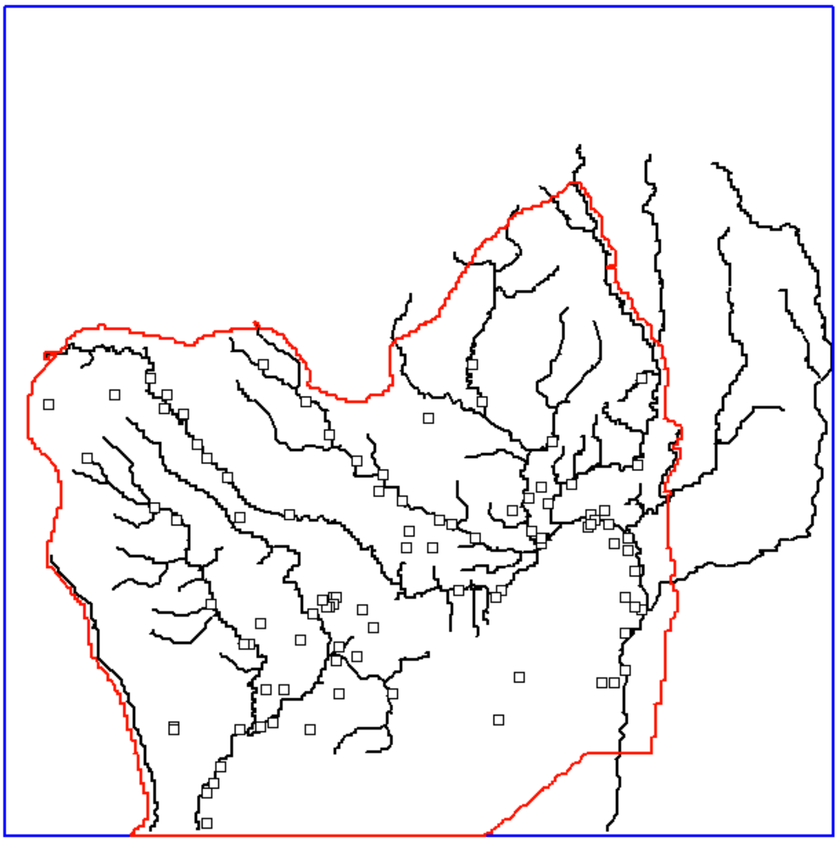


Figure 7.6: Distribution of stream cells (black lines) and wells (black squares) in the NNRM, the active boundary (red line) and entire model domain (blue line) are also shown

applied to all stream cells, the stream bed conductance was varied between 0 - 1600m^2/day depending upon the conceptual model, the underlying geology and whether the river was considered effluent or influent and that location (Buckle, 2005). The lower reaches of the Mym

Abstraction data for 98 locations were compiled from Water Utility and Environment Agency records, initially for the ULMM were directly imported into the BGFM (Buckle, 2003). The NNRM used the same abstraction nodes as were defined for the BGFM and the ULMM although the datasets for such abstractions were updated to 2004. The NNRM also included abstractions at the NNR wells which were omitted from the BGFM as the NNR well field was located outside the boundary of the active model (Buckle, 2005). The distribution of modelled abstraction wells is presented in Figure 7.6.

Initial heads in the ULLM, BGFM and NNRM were based on interpolation of spatial head distributions in 1998 (Buckle, 2005). 1998 was a year of groundwater recovery following a drought in preceding years (CEH, 2006). The ULLM uses minimum groundwater levels from January 1998 and the BGFM and NNRM used average heads from December 1998. In January 1998 in Hertfordshire, observation wells still indicated notably low levels. By December 1998 groundwater levels in Hertfordshire had recovered to long term average levels (CEH, 2006). An alternative approach would have been to derive long term heads by running a steady state groundwater flow model as recommended by Reilly and Harbaugh (2004) to avoid problems with convergence of the model. However, there is no indication that steady state modelling was undertaken to determine average long term heads for a baseline comparison with any of the models or to derive input data.

7.2.2.2 Fidelity of the Argus ONE NNR replicate

Having duplicated the NNR input data within the Argus ONE GUI, verification of the model is required to ensure that the duplicate is free from error, both human and computational, since the Argus ONE has a different method of representing and producing MODFLOW output.

Spatial distribution of heads at key calibration times for the Buckle (2005) NNRM and the replicate model are presented in Figure 7.7. The transient modelled heads at key calibration points located close to the centre of the Bromate "plume" are presented in Figure 7.8. The replicate NNRM nearly exactly reproduces the spatial distribution and temporal variation of heads at calibration points demonstrating that the implementation of the NNRM with the Argus ONE GUI has been achieved. This allows development of a new model using the NNRM as a baseline case.

The temporal plots in Figure 7.8 also indicate the quality of the NNRM at replicating observed heads; in general a good calibration is achieved at these locations, however one shortcoming of the model is highlighted: the effect of droughts in 1992 and 1997 are over-estimated by the models. This effect is most apparent at locations within the Vale of St Albans and probably relates to insufficient model storage and therefore pore representation of the buffering of groundwater recession by the glacial gravel deposits in the Vale.

7.2.3 Development of a Subset Model

The working replicate of the NNRM makes apparent several potential problems for any derivative.

- The model execution times were on the order of 2 hours for the MODFLOW flow model and 4-5 hours for the MT3DMS transport model, increasing computational resources and restricting the ability to make numerous changes or automated calibration of the model
- The large data requirements of the model, particularly relating to recharge stress and stream boundary conditions occasionally made the GUI unstable and the exporting of model data was computer intensive
- The MODFLOW and MT3D model itself is unstable and minor changes could often result in non-convergence

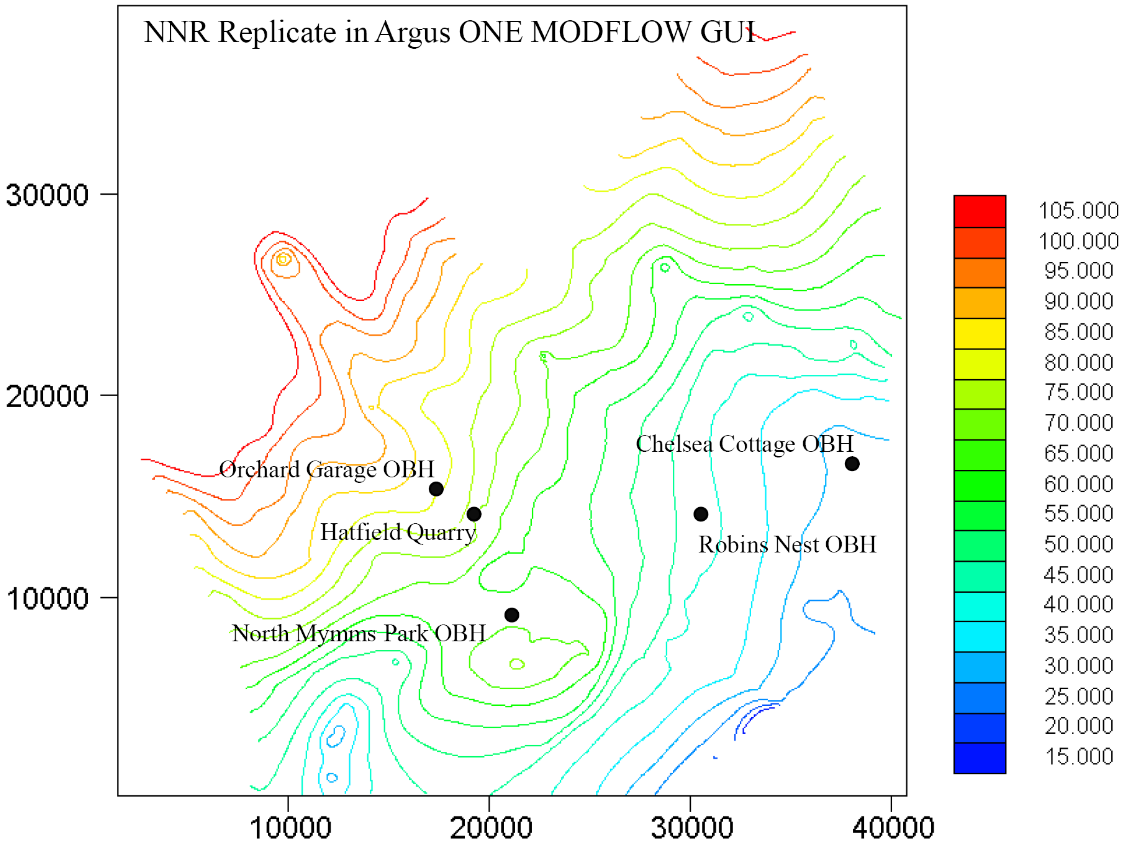
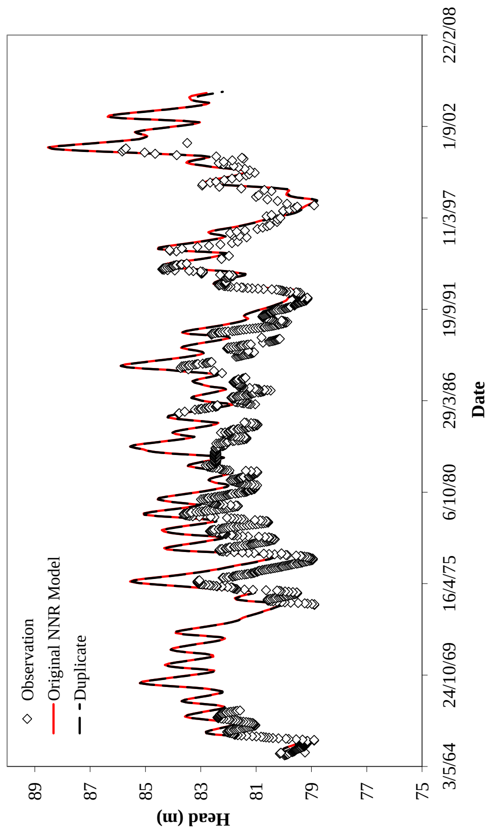
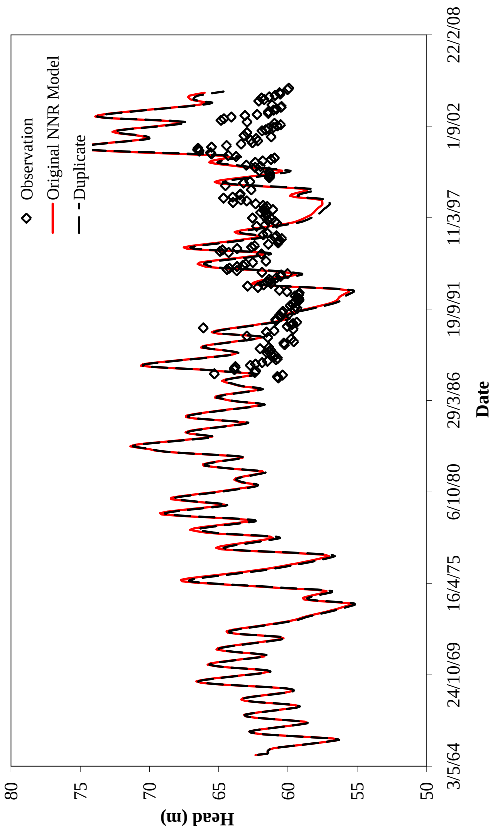


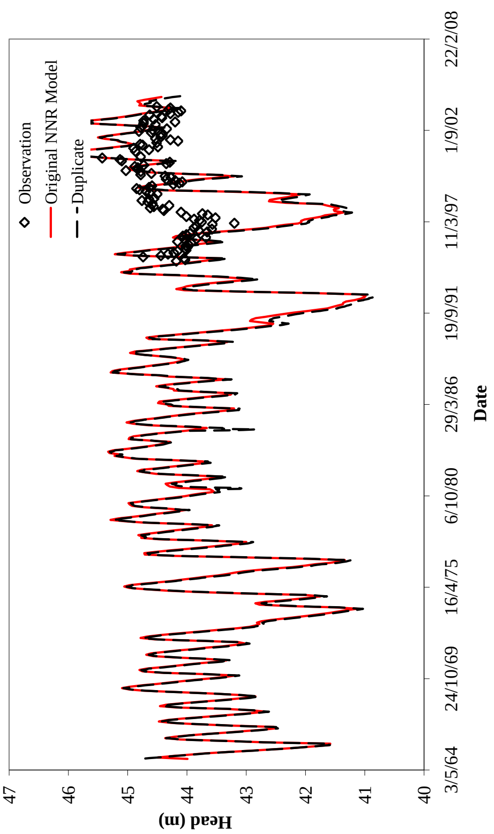
Figure 7.7: Verification of successful implementation of the NNRM within the Argus ONE GUI demonstrated by the spatial variation of heads (October 2000) to be compared to those provided in (Assem, 2005; Buckle, 2005), observation points where time series data are presented are indicated.



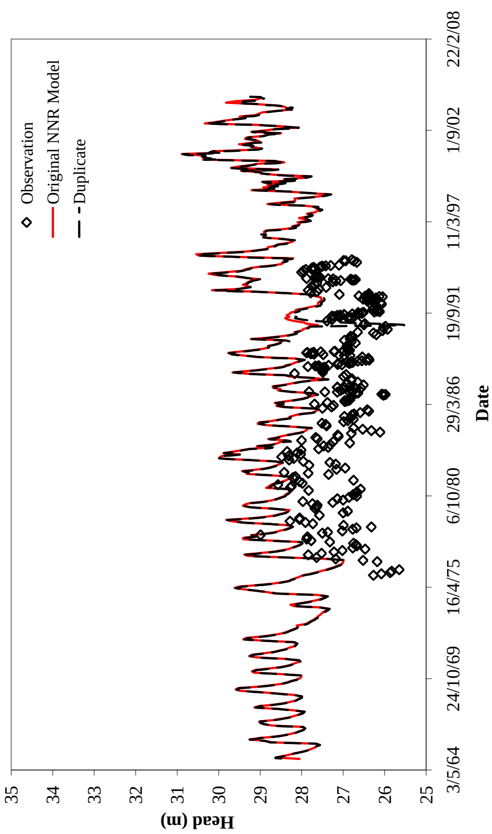
(a) Amwell Corner



(b) North Mymms Park



(c) Robins Nest



(d) Chelsea Cottage

Figure 7.8: Verification of successful implementation of the NNRM within the Argus ONE GUI demonstrated by temporal variation of heads at key calibration points located close to the apparent bromate "plume" - the locations of the calibration points are presented in Figure 7.7.

To facilitate easier modification of the model a steady state subset model was developed which would allow faster execution times, simpler initial calibration to long term heads and flows and improved model stability. Haitjema (1995, 2006) suggests that under certain circumstances steady state groundwater flow models can be as effective as transient models, particularly where the contribution of storage is negligible on the time scale in question and the value of a dimensionless parameter τ (Equation 7.1) is ≥ 1.

$$\tau = \frac{SL^2}{4kbP} \tag{7.1}$$

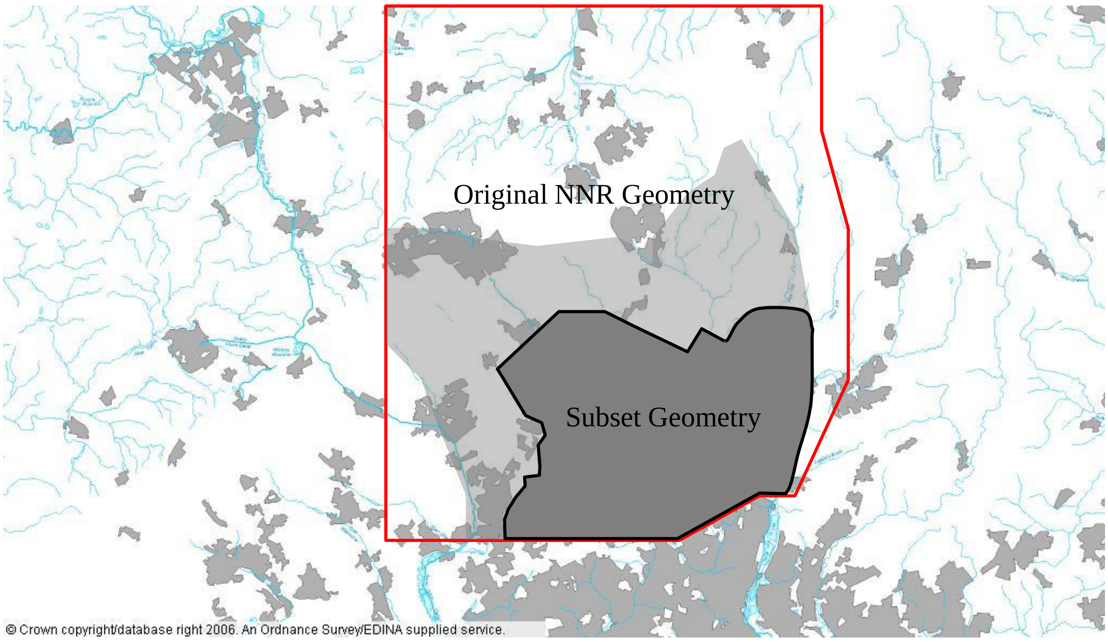
Where S is the Storativity, L is the average distance between surface waters (effectively the catchment width), k is the hydraulic conductivity, b is the effective aquifer thickness and P is the period of the forcing fluctuation, taken to be 365 days for seasonal fluctuations. Adopting typical values for the Chalk for S of 0.03 and k of 3m/day for the Chalk interfluves and 150m/day for the karst zone, and b=60m (Buckle, 2005), and L of 3500 - 5500m which is the range of spacing between the Rivers Ver, Lee, Mimram and Beane, implies τ is in the range of 1.4 - 985 for interfluves of the Hertfordshire Chalk, although for Hertfordshire the value of τ is marginal, and taking all modelled parameters into account τ could be as low as 0.2, in which case a transient model is appropriate. To account for this variation, initial calibration will be undertaken using steady state stresses but to ensure transient factors are not neglected comparison was made against a transient model, following the approach adopted by (Scanlon et al., 2003).

Input stresses for cells containing wells, recharge and stream flows for the steady state model were derived by determining long term average input data from the original NNRM inputs.

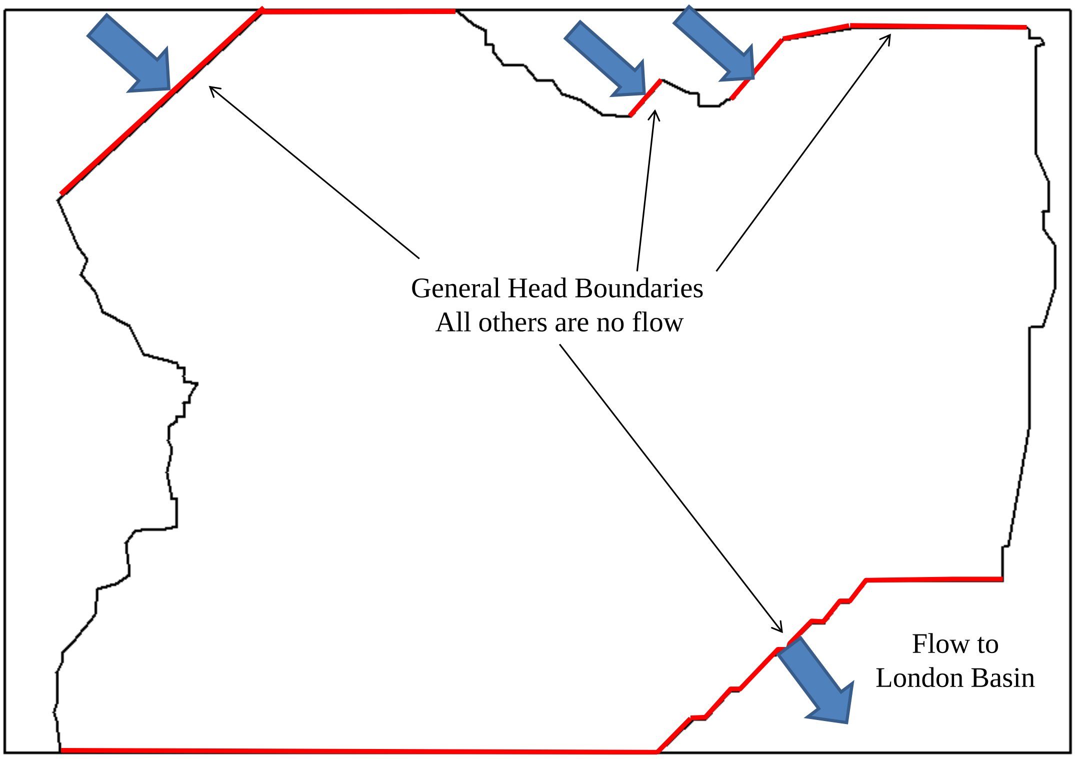
To further reduce the data requirements and improve computational efficiency a subset model grid was also developed. The area of the subset is presented in Figure 7.9 and has been adopted to be approximately coincident with that of the BGFM in the south and east. The original 200 x 200m grid discretisation of the NNRM was retained within the subset model. The area of the subset model is also approximately coincident with that for which a water balance is described in Section 6.3.

The subset reduced the model grid to 16740 cells in 155 columns and 108 rows of 200m width and height, compared with 62500 cells in the original NNRM. The approximate spatial extent of the subset model extends from NGR 510000 195000 in the south west to NGR 541000 216600 in the north east. The southern boundary of the NNRM was retained but slightly shortened. Whilst the extent of the model grid has been reduced in the east all the cells removed cells were designated as inactive in the NNRM and the original eastern no-flow boundary has be retained.

Modifications were made to the model boundaries in the North and west of the Model. In the west a no flow boundary was added along a flow line coincident with



(a) Subset area of the NNRM



(b) Lateral boundaries of the subset model

Figure 7.9: [Boundaries of the subset model]Relative spatial extents and boundary conditions of the subset NNRM compared to the original

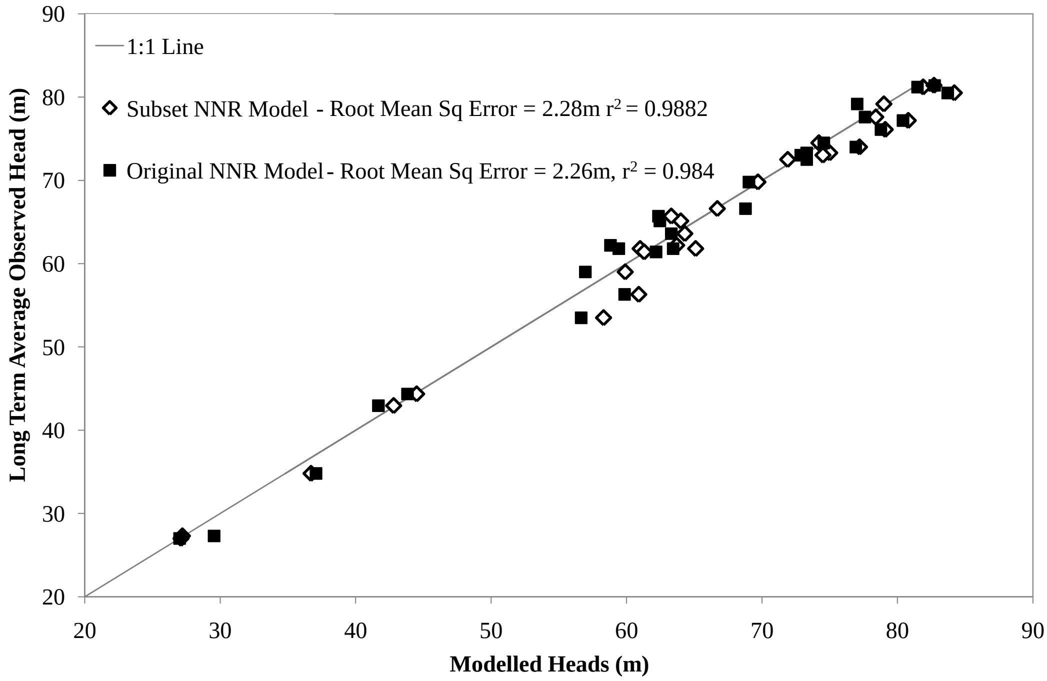


Figure 7.10: Comparison of average observed and modelled heads for the steady state NNR subset model and long term average values from the original NNRM of Buckle (2005).

the River Ver to allow only flow occurring parallel to the model boundary.

The northeastern boundary of the model was defined at the approximate location of 90mOD groundwater contour since this is distant from the principal region of interest between Sandridge and the Lee Valley. Since the regional piezometry and the NNRM indicate that flow occurs in a south-east direction across this arbitrary boundary, a general head boundary condition was simulated. Boundary heads were assigned based upon long term piezometric data provided in Buckle (2002) and a high conductance of 300m/day to allow modelled heads to be approximately equal to imposed boundary heads.

In the north a no-flow boundary was assigned parallel to a flow line coincident with the River Mimram between Welwyn and Panshanger, similar in form to the BGFM, however close to the confluence of the Mimram and Lee the contribution of groundwater form the north exerts an influence. A further general head boundary condition was defined at the approximate location of the 45m and 40m groundwater contours.

Piezometric head data was available for 29 locations within the active area of the sub-set model. The spatial distribution of modelled heads and observation points for the subset model is presented in Figure 7.11 and Figure 7.10 shows modelled steady state heads plotted against long term average heads for observation data, and for the same locations in the original NNRM.

Head data show a good fit to long term average data for the subset model with a Pearson's correlation coefficient of 0.97 although, the original NNRM does show

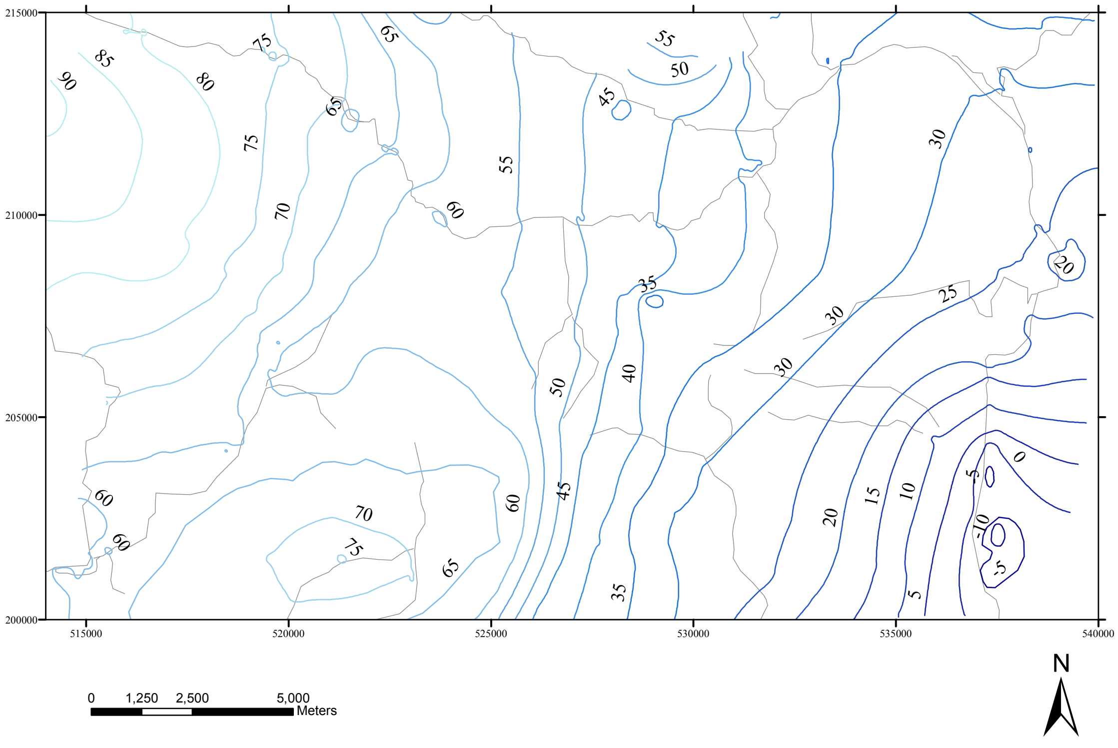


Figure 7.11: Steady state simulated piezometric heads (mOD)in the subset NNRM derived from modeling long term average stresses for the period 1965-2004, based upon data provided in the parent model by Buckle (2005).

Table 7.3: Comparison of steady state flows across the general head boundaries in the north of the subset NNRM to the long term average transient values derived from the original NNRM of Buckle (2005)

Model	Flow Across Boundary (Ml/day)		
	North West	Mimram	North East
Original NNR (Buckle, 2005)	12.61	2.58	13.64
Subset NNR	12.51	2.68	13.58

a slightly improved statistical fit. The general spatial pattern of groundwater levels is also replicated, including the North Mymms Recharge Mound (Figure 7.11).

The general head boundaries in the north and south of the subset model represent relatively arbitrary locations. To ensure that flows across these boundaries are realistic, calibration of the defined heads and conductance has been undertaken to ensure that flow across the boundary is comparable to the range of flows at these locations determined from the original NNRM and flows are presented in Table 7.3. Tests indicated that modelled heads near the centre of the model are not sensitive to the general head boundary flows and the position of the boundaries does not influence heads and flows in the region of interest relating to bromate transport.

Further validation of the subset model is possible by reference to river flows, calculated using the Stream Flow Routing package of Prudic (1989). (Table 7.4). Modelled flows are all within the range of observed flows derived from river gauging, as in the NNR Model. The largest discrepancy exists for the River Lee at Water Hall

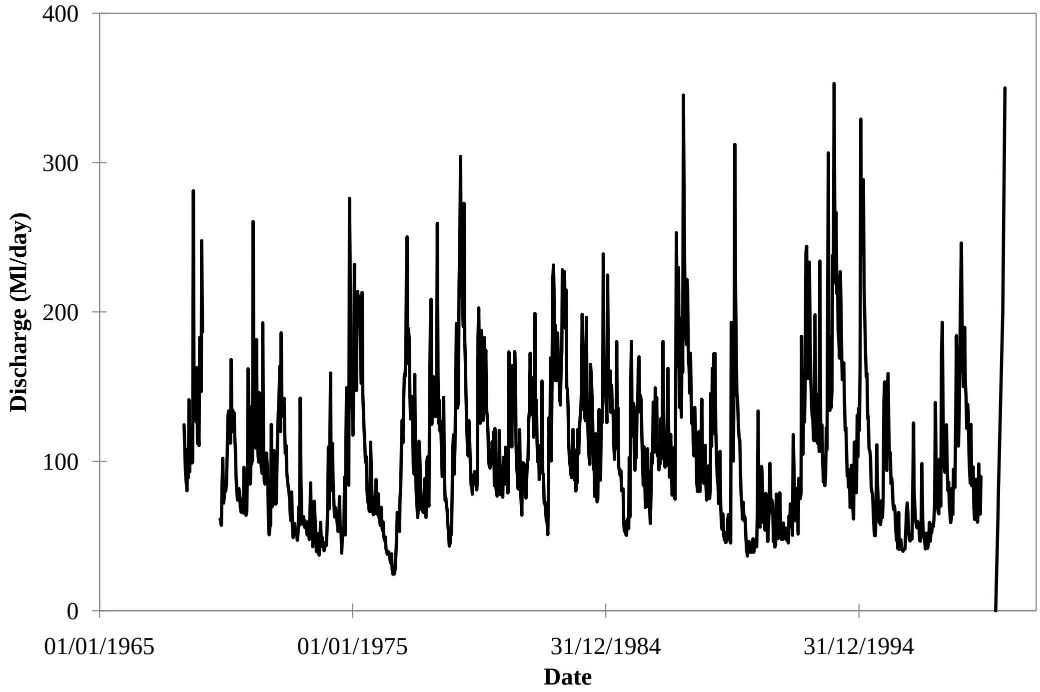


Figure 7.12: Gauged flows in the River Lee at Water Hall, data is from Assem (2005)

Table 7.4: Comparison of simulated stream flows in the subset model with gauged data and the parent NNRM of Buckle (2005). Gauged flow data are taken from (Assem, 2005)

Location	Flows (Ml/day) Gauged 1970-1998			NNR Model		Subset model	
	Min	Max	Mean	Mean	Residual	Steady State	Residual
River Lee							
Water Hall	24.4	352.9	107.1	106.1	1	79.9	27.2
Rye Bridge	22.9	2038.9	244.1	226.7	16.2	238.1	6
R. Mimram							
Panshanger	12.3	120.7	43.3	41.1	2.2	59.1	-15.8
River Ash							
Easneye	1.27	311.7	25.1	20.9	4.2	20.9	4.2
River Ver							
Hansteads	0	122.3	31.2	18.7	12.5	42.1	-10.9

gauge with the subset model underestimating the long term mean flow. Examination of the time series data at this location presented in Figure 7.12 indicates that the majority of flows are between $60 - 80Ml/day$ and higher flows $\geq 100Ml/day$ occur less frequently only during winter peaks, probably reflecting increased run-off which is not accounted for in the modelled long term recharge stress, but is of sufficiently high volume to affect the long term average. The steady state subset modelled value of $79Ml/day$ is probably a reasonable representation of the base flow contribution of groundwater during summer months.

Establishing a subset steady state model has reduced the complexity of the original NNRM, and as a consequence has improved the model stability, reduced computational effort and processing time. Comparison with calibration data for the original model indicate that there has been only a slight decrease in goodness of fit of the model to observed head and flow data. Since the NNR subset model provides an approximate replication of the head and flow distribution of observed data and the parent model it is considered to be an acceptable baseline case for further model development to include karst features and solute transport.

7.3 Incorporating the Hertfordshire Karst in the Subset Model

The incorporation of karst features into the subset model resulted in a major alteration of the hydraulic parameters and as a consequence changes to the distribution of heads and flows.

7.3.1 Hydraulic Conductivity

The principal aquifer parameter of interest in determining a suitable karst representation of the aquifer under steady state conditions is the distribution of hydraulic conductivity, since this directly influences both the flux and piezometric head within the model. The distribution of hydraulic conductivity in the parent NNRM of Buckle (2005) presented in Figure 7.4 illustrates the shortcomings in the previous representation of the Hertfordshire karst.

In EPM representations of karst aquifers, model cells containing karst conduits are assigned values of high transmissivity or hydraulic conductivity to represent the conduits contained within. Such an approach has generally proved successful at simulating heads and fluxes, however the major criticism of EPM models is that they are unable to represent the heterogeneity in terms of the direction and velocity of solute transport (Quinlan et al., 1996) quoted in Scanlon et al. (2003). The NNRM is one such example of a model that is reasonably well calibrated to heads and flows but which fails to reproduce the transport velocity and connections established by the Karst system. This is demonstrated in Figure 7.13 which shows the simulated destination and travel time of particles released at Water End, Sandridge and the Catherine Bourne using the MODPATH particle transport package (Pollock, 1994) with the NNR subset model. The model is able to replicate some of the general features of the karst system in that the majority of particles input at water end travel North then East approximately coincident with the Palaeocene feather edge, but the travel times are longer than those observed.

The extent of the bromate contamination, the catchment-scale tracer testing and the inferred conceptual understanding established for the Hertfordshire Chalk aquifer provides an improved basis on which to calibrate a groundwater flow and solute transport model of the aquifer.

The initial modified distribution of hydraulic conductivity was based upon the

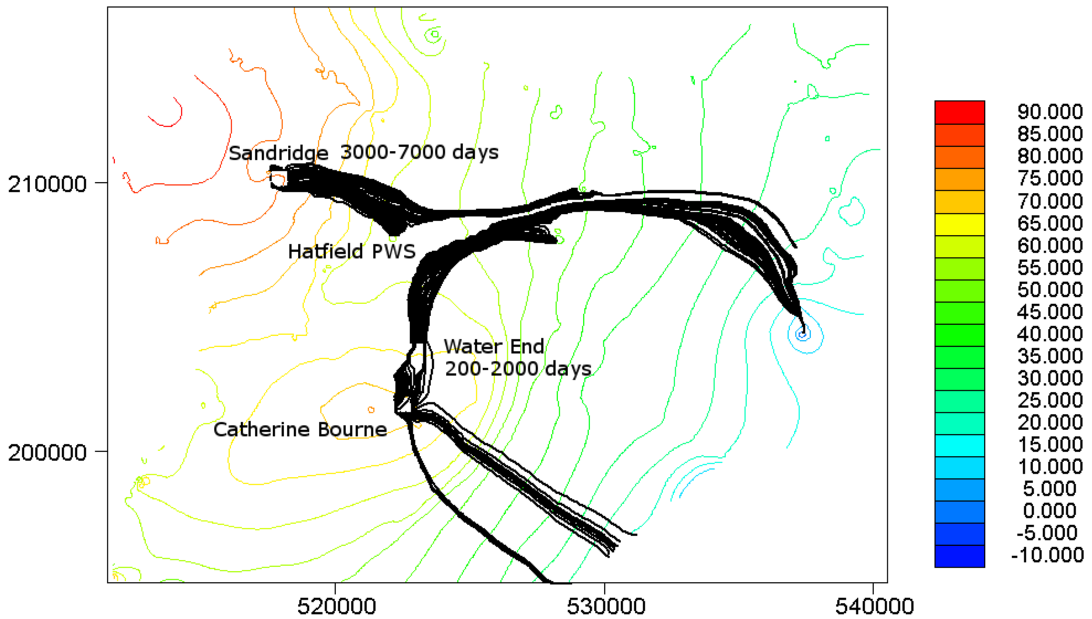


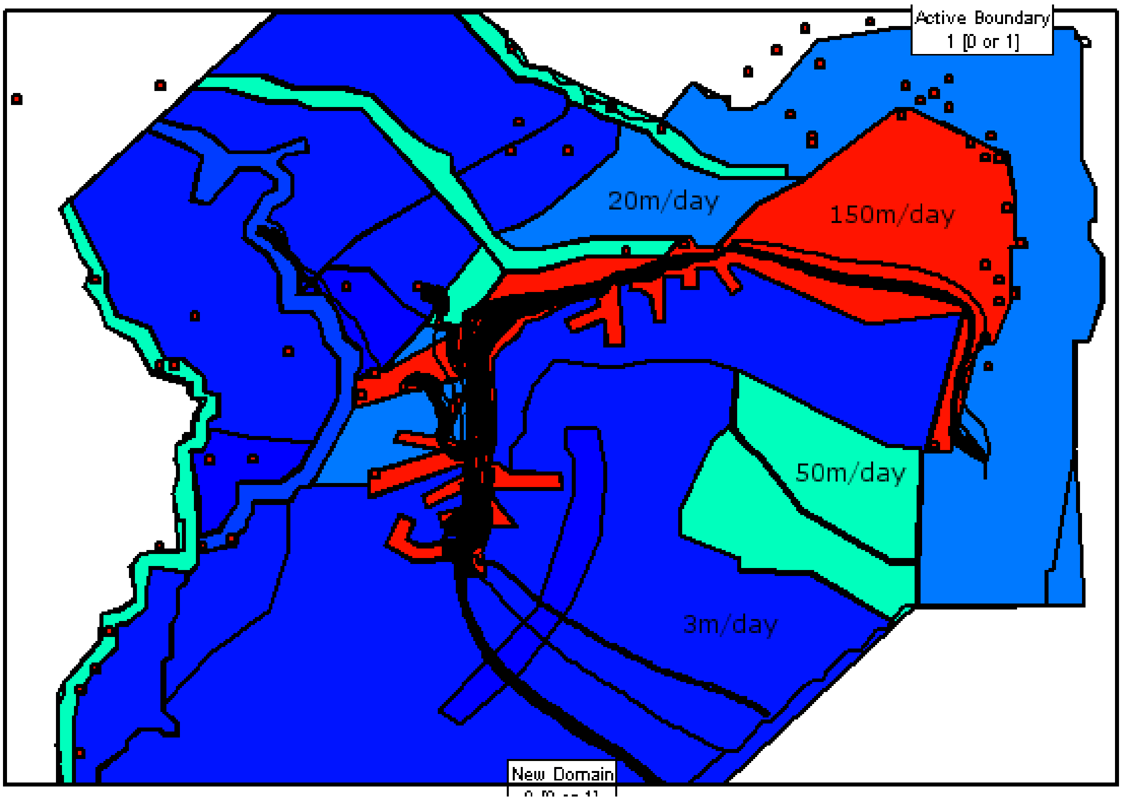
Figure 7.13: MODPATH forward particle tracks indicating advection directions and travel times to the Lee Valley for the NNR subset model. Although the modelled flow paths capture flow from Sandridge to Hatfield and the flow from Water End along the approximate location of the Palaeocene Feather edge, travel times are longer than indicated by the tracer testing and no connection is established with the Lee Valley.

inferred geometry of the karst conduits and is presented in Figure 7.14. The majority of the NNR hydraulic conductivity distribution outside the main karst zone has been retained since the NNRM provides a reasonable representation of heads and flows in these areas and there is no currently available indicating the existence of karst flows in this regions. In some areas, particularly relating to the area in the north west of the model and beneath the London Clay the hydraulic conductivity distribution was simplified and merged to further reduce model complexity and increase model parsimony.

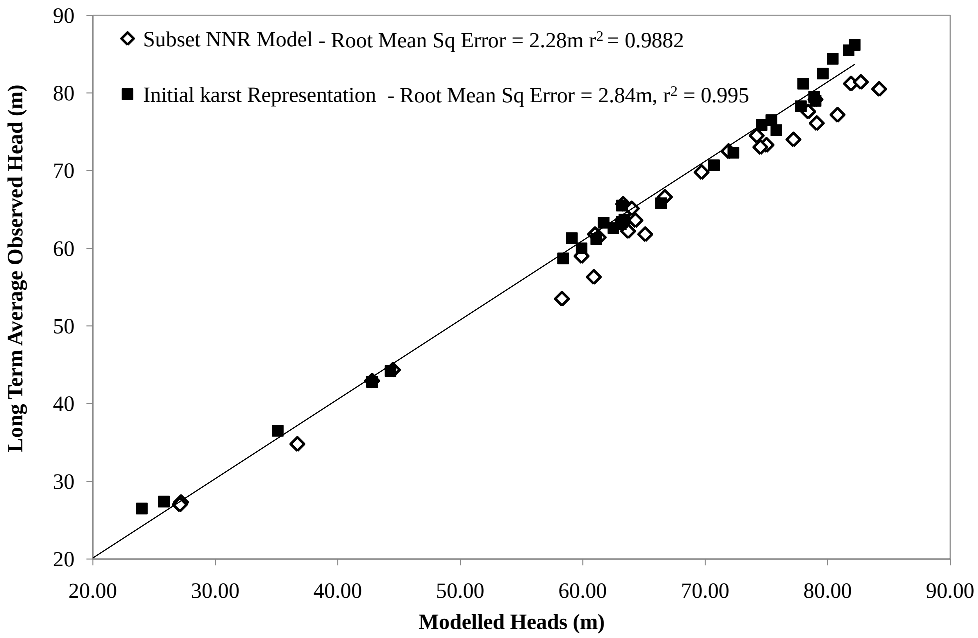
This initial replication of the karst geometry gives a slightly poorer fit to observed heads than both the parent NNRM and the subset NNRM (Figure 7.14). The MODPATH path lines do indicate a slight improvement over that of the original NNRM, with particle tracks extending from Water End to the approximate area of Turnford PWS. However the path lines from Sandridge no longer reach Hatfield PWS and are orientated further south.

To improve the model fit, the built-in parameter estimation package of MODFLOW-2000 was used to derive hydraulic conductivity values that provide the best fit to observed data for a hydraulic conductivity distribution which incorporates the inferred geometry of karst development. The automated calibration was able to improve the model fit to observed long term piezometric head suggesting an increased hydraulic conductivity for the karst zone of 390m/day.

The automated calibration resulted in a improved fit to observed steady state heads compared to the initial representation of the karst geometry, the parent NNRM



(a) Hydraulic Conductivity Distribution



(b) Piezometric Head Calibration Plot

Figure 7.14: Calibration performance and Initial hydraulic conductivity and MODPATH pathline representation of the Hertfordshire Karst. The inferred conduit geometry has been defined as a narrow zone of relatively high hydraulic conductivity following the surface distribution of swallow holes and the Palaeocene feather edge. The initial value for hydraulic conductivity in the karst zone is based upon the highest value adopted for karst in the NNRM (150m/day). When compared with the NNR hydraulic conductivity distribution in Figure 7.4 many areas have also been simplified.

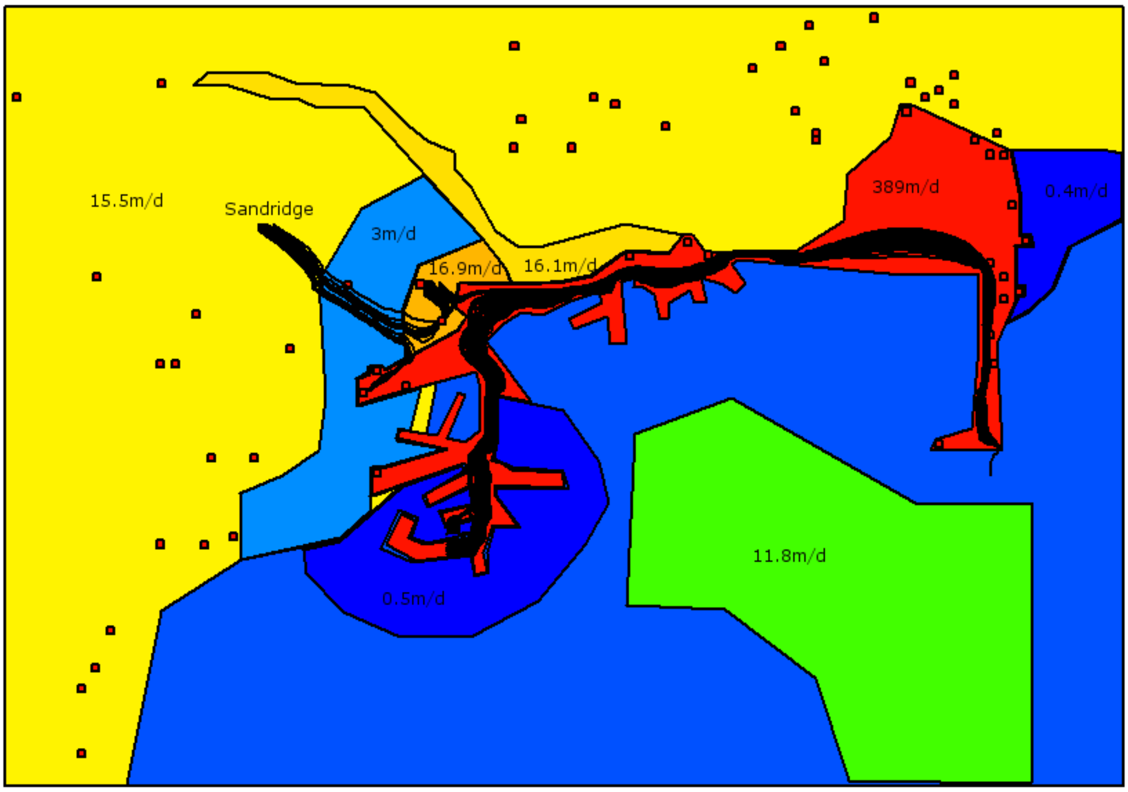


Figure 7.15: Best fit hydraulic conductivity distribution for the simplified model geometry and associated forward MODPATH path lines from Sandridge and Tracer injection locations.

and its subset. The representation of MODPATH path lines is also improved within the karst zone indicating flow from Water End and the Catherine Bourne reaches the Lower Lee Valley. However, flow paths from Sandridge are less well modelled, reaching Tyttenhanger PWS rather than the Hatfield area and the simplification of the model parameters and geometry within the Vale of St Albans has had detrimental effect on the direction of flows.

Since the principal modelling aim is to replicate transport rather than heads and flows, the best fit distribution of hydraulic conductivity was subsequently modified at the expense of the quality of the head calibration in order to calibrate flow paths more closely to those observed from the tracer tests. In particular, replicating the connection between Water End and the Lee Valley and the connection of Sandridge area to the Lee Valley. The Forward tracking of particles from the tracer injection locations was used in combination with backward tracking from connected locations. A summary of the calibration changes made are presented in Table 7.5.

Table 7.5: Summary of calibration changes made to Hydraulic conductivity distribution

Revision	Changes Made	Sum of Square Residuals (Heads)	Root Mean Square Error(m)
NNR Replicate	Replicate of Atkins Model	155.7	2.28
NNR Subset	Creation of a subset model, approximate replication of parent model	153.6	2.26
Initial Karst Geometry	Simplified hydraulic conductivity distribution and added karst geometry	241.8	2.84
Automated K Estimation	PEST package used to determine best fit K	95.24	1.78
Rev 1	Added NNR discretisation back to Vale of St Albans and some confined Chalk areas	219.4	2.70
Rev 2	Changes to area around North Mymms and confined Chalk	163.1	2.33
Rev 3	Minor change to karst geometry in the Water Hall area	199.2	2.58
Rev 4	Added additional low K zone along Lee Loop to prevent flowpaths terminating in the river	209.2	2.64
Rev 5	Further revision to geometry of Karst zone in the area of Brickendonbury	207.1	2.63
Rev 6	Extension of karst zone to Lynchmill Spring	208.4	2.64
Rev 7	Further alternation in Brickendonbury area, reduced k of karst zone	233.4	2.79
Rev 8	Increased k of karst zone	182.5	2.47
Rev 9	Minor change to karst zone at Arkley Hole, narrowed karst geometry near Hatfield	182.5	2.47
Rev 10	Minor change to karst zone at Arkley Hole	181.2	2.46
Rev 11	Further narrowing of karst zone at Hatfield	180.55	2.45
Final	Minor adjustment in area of North Mymms	108.2	1.90

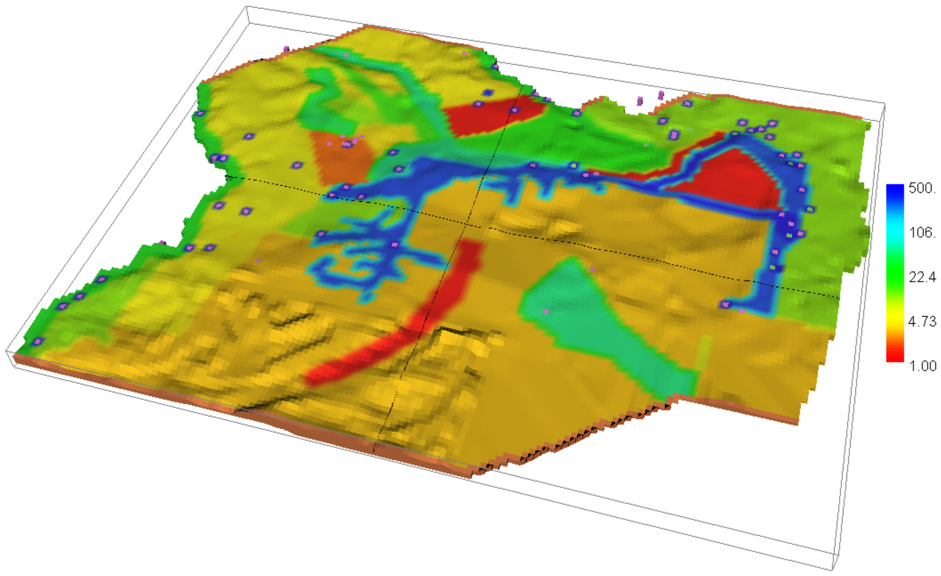


Figure 7.16: Distribution of hydraulic conductivity for the calibrated karst EPM representation in MODFLOW.

The final calibrated pattern of hydraulic conductivity, heads and flow paths are presented in Figure 7.16 and Figure 7.18. The calibration procedure has not only improved the statistical fit to heads when compared to the original NNRM but has also incorporated a representation of the karst geometry, consistent with that of the conceptual understanding, and provides approximately correct flow path connections. The general spatial distribution of observed heads and flows has remained relatively unaffected.

The overall magnitude of the hydraulic conductivity vales in the calibrated model have not been changed from the range of the original NNRM except within the karst zone. Adopted values are generally in the region 0.5-50m/day for much of the model (an equivalent transmissivity of 30-3000m^2/day for 60m of effective aquifer) which is broadly consistent with the range of observed values in the Hertfordshire Chalk (see Chapter 3 and (MacDonald and Allen, 2001). The overall geometry of the hydraulic conductivity distribution has also been largely retained, particularly the general geomorphological pattern of high hydraulic conductivity in valleys (20-50m/day), relatively low on interfluves (1-20m/day), and lower still in the Chalk underlying the London Clay (0.5-3m/day). Within the karst zone itself values of between 300-550m/day were required in order to achieve a satisfactory distribution of flow paths, equivalent to a transmissivity of 18,000-33,000m^2/day. Higher values tended to result in non-convergence of the model. Smaller values resulted in a poorer fit to the flow path and head distribution.

The forward and backward flow paths for the calibrated karst EPM representation are presented in Figure 7.18. Since the transport of MODPATH particles occurs by advection along flow lines only, there are limitations to the extent to which actual

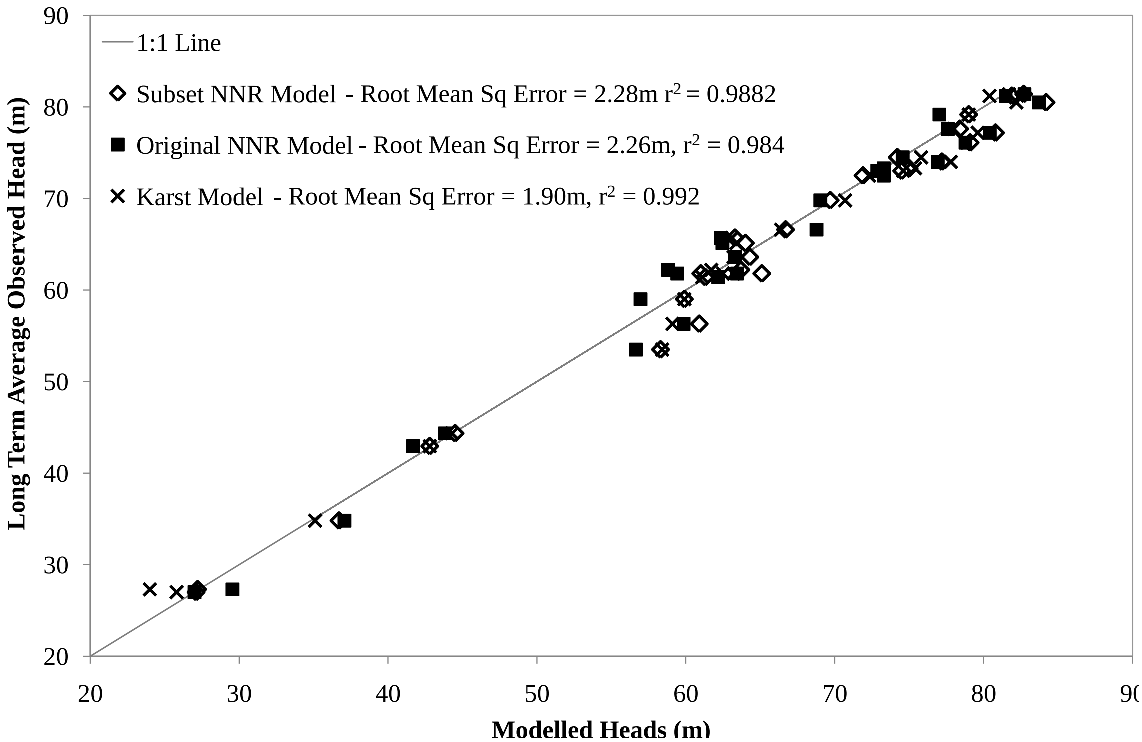


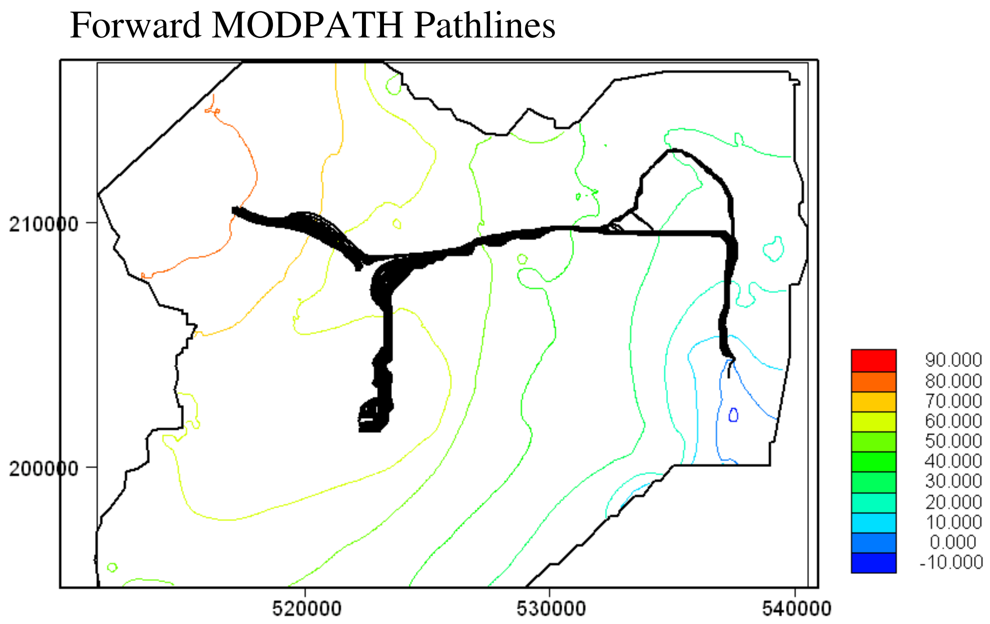
Figure 7.17: Comparison of simulated and observed heads for the karst EPM model and NNRM

flow paths and connections can be defined since, in reality, dispersive processes will affect the distribution of transported solutes. Flow paths cannot be made to cross and the resolution of the grid and number of particles impose additional restrictions. Despite these limitations the general pattern of the flow paths replicates most of the essential features of the karst system:

- The Water End and Mymmshall Brook area is connected to the Lee Valley via a flow path developed along the karst zone of the Palaeocene boundary.
- Forward and backward tracking indicates flow routes follow the River Lee and the inferred "short cut" to the Lynchmill Spring and Hoddesdon Area.
- Most of the modelled flow paths from the Sandridge area across the Vale of St Albans are captured by Hatfield PWS although a proportion bypasses the abstraction point to the north reaching Essendon PWS, Arkley Hole and the Lee Valley.
- The inferred short cut to Turnford PWS due east from the Mymmshall Brook catchment is also indicated

7.3.2 Representation of Springs

Major karst spring features were not included within the original NNRM. As discussed in section 7.1 spring features are often represented in equivalent porous media



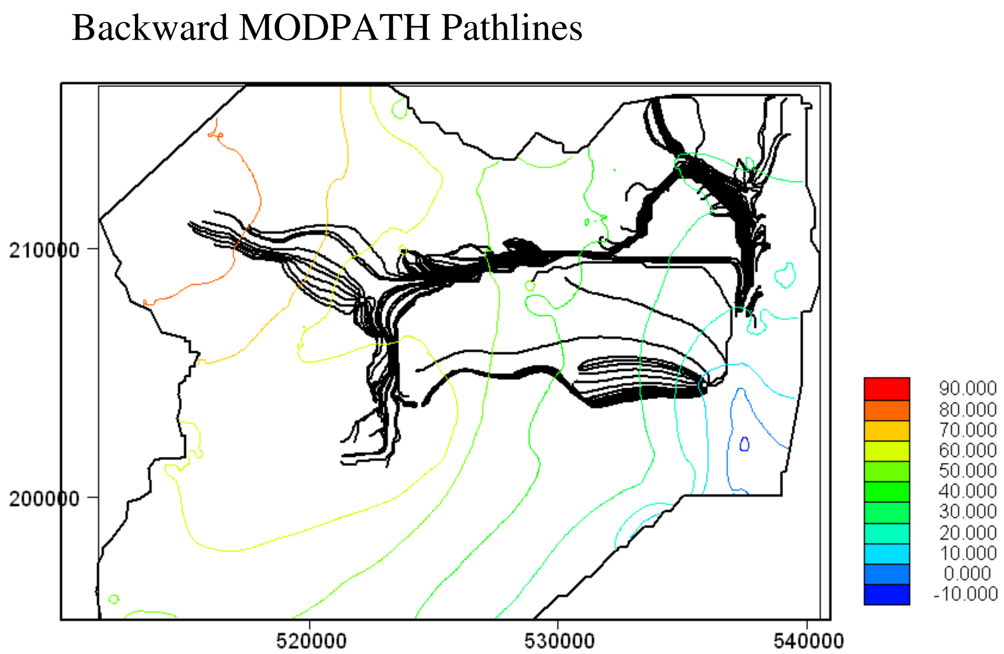


Figure 7.18: Forward and backward flowpaths using MODPATH in the calibrated karst EPM model indicate that the general features and connections of the karst conceptual understanding have been captured by the model characterisation

Table 7.6: Spring flows were calibrated in the karst by adjusting the elevation of the drain. The initial elevation was taken as top the of the active model aquifer layer.

Spring	Observed Discharge (Ml/day)	NNR subset Elevation (mOD)	NNR subset Discharge (Ml/day)	Calibrated Karst Elevation (mOD)	Calibrated Karst Discharge (Ml/day)
Arkley Hole	6.00	47	0	45.04	6.05
Chadwell Spring	5.0	36.8	0	28.5	4.99
Emma's Well	2.0	29	0	26.39	1.92
Lynchmill Spring	4.0	22.8	1.06	22.54	4.08

MODFLOW type models through the use of the drain package (Scanlon et al., 2003; Quinn et al., 2006, e.g.). The drain package was originally developed to model the behaviour of agricultural land drains and allows linear one way discharge from the aquifer based upon relative difference in elevation between modelled heads and the elevation of the drain cell (Harbaugh and McDonald, 1996) and moderated by an assigned boundary conductance.

To simulate the behaviour of springs and allow discharge from the aquifer at these locations, single cell drain boundaries were added to the model at the geographic positions of major springs. The elevation of the springs was defined at ground level (see Section 6.1.2) and a high cell conductance of 10000m^3/day was assigned to allow nearly unrestricted drainage out of the spring following the approach of (Scanlon et al., 2003). The spring discharge was calibrated by adjusting the drain cell elevation was adjusted until a close agreement with observation data was achieved (Table 7.6.

The use of drain cells can only provide a limited representation. The Hertfordshire springs occur at the downstream termination of karst conduits which cannot be discretely represented within an EPM type model. Actual discharge at the spring is determined by the upgradient pressure and recharge entering the conduit network, whilst in the MODFLOW model discharge is determined by the local head conditions adjacent to the stream cell and whilst this allows outflow from the aquifer at the correct location, the actual conduit flows can only be approximated and must rely on the definition of other model parameters.

7.3.3 River Flows

River flows generated by the inclusion of Stream Flow Routing (SFR) cells in the karst model are presented in Table 7.7. The overall fit to stream flows has also been slightly improved at all locations relative to the subset NNRM despite no direct efforts to calibrate to stream flows.

Table 7.7: Comparison of simulated stream flows in the calibrated karst model with gauged data and the subset NNRM. Gauged flow data are taken from (Assem, 2005)

	Flows (Ml/day)		
Location	Gauged 1970-1998	NNR Subset	Karst Calibrated
R. Lee at Water Hall	107.1	79.9	98.5
R. Lee at Rye Bridge	244.1	238.1	253.8
R. Mimram at Panshanger	43.3	59.1	49.2
R. Ash at Easneye	25.1		23.2
R. Ver at Hansteads	31.2	42.1	42.0

7.4 Simulation of the 2008 Tracer Tests

An approximation of the major karst flow paths by an EPM approach has been integrated into a calibrated groundwater flow model, which can now be adapted for the simulation of solute transport. The MODPATH flow routes have already shown that advective transport routes for the Hertfordshire Karst system will be approximately correct; these are developed through additional parameterisation of the aquifer so that the concentrations and travel times of transported solutes is appropriate.

Tracer travel times and karst flow velocities have been evaluated through the use of the effective porosity parameter and checked using the advective MODPATH package. Following the methodology adopted for the hydraulic conductivity calibration a zone of low effective porosity was defined following the same spatial geometry as the karst zone and the effective porosity parameter was adjusted until travel times were replicated to within ±1 day of that indicated by the tracer testing. An effective porosity value in the region of 0.006-0.008% provided the best fit to observed data with travel times of 3-4 days between Water End and Arkley Hole and 4-13 days to Lynchmill Spring and are consistent with the tracer test data .

The estimated effective porosity values are much lower than those typically observed for the Chalk. Partly this reflects a limitation of the EPM approach whereby flow velocities are determined by Darcy's law, i.e. the relative ratio of the specific discharge and effective porosity, and must be defined as such across the whole of the model cell, in effect, a single karst conduit might be represented by a model cell some 200m x 200m x 60m in size. An additional problem is that the relative values of hydraulic conductivity and effective porosity that would yield flow velocities in the desired range are non-unique and are in fact limited by the stability of the model at higher hydraulic conductivity or lower effective porosity. Since the adopted hydraulic conductivity value has provided good calibration to heads and flows, what is crucial for the transport model is achieving the correct value for the defined conditions that will provide advective flow velocities within the range of that observed for the aquifer.

Although low, the estimated effective porosity values on the order of 7×10^{-5} are not necessarily unrealistic and would equate to an equivalent effective pore volume of $168m^3$. Assuming that pore volume is a single cylindrical conduit extending 200m across an entire model cell it would have an equivalent cross sectional area of $0.84m^2$ and diameter of 0.52m which is within the range of that observed for Chalk karst conduits (**??**). Similarly, assuming a set of plane parallel fractures, a spacing of 10m and aperture of 1mm leads to an effective porosity of 5×10^{-5}.

Transport has been simulated using MT3D-MS version 5.1 (Zheng and Wang, 1999). The transport parameters have been calibrated by developing simulations of the 2008 tracer tests, initially of the Water End injection and subsequently the injections at Comet Way, Hatfield and Harefield House OBH, Sandridge.

The rapid flow velocities and low dispersion required to simulate karst transport are likely to cause some numerical dispersion in transport models. In order to minimise dispersivity, the cell dimension (dx) should be such that the Peclet criterion (dx/α_x) is ≤ 2 (Pinder, 2002) where α_x is the dispersion length (dispersivity). For the Hertfordshire karst model, with a cell dimension of 200m the Peclet criterion is in the range 2-20 for the values of dispersivity suggested by the tracer testing. Additionally the Courant criterion (equation 7.2) defined as the ratio of advective distance to cell dimension (Spitz and Moreno, 1996) should be ≤ 1 so that transported species cannot move more than one cell per transport time step.

$$C_0 = \left| v \frac{dt}{dx} \right| \tag{7.2}$$

To minimise the effect of numerical dispersion on simulation the "3rd Order total varying diminishing" (TVD) solver was used which is both mass conservative and minimises numerical dispersion in advection dominated problems (Zheng and Wang, 1999). This automatically imposes the Courant Criterion limit with a simulation time step of approximately step 2.75×10^{-3} days (3.89 minutes). During selection of a solver, the TVD solver was compared against the Method of Characteristics (MOC) solver which also has low numerical dispersion. however, on the basis of mass balance the TVD solver was found to provide better performance (see Appendix D).

A two region (mobile and immobile) dual porosity model approximated by a first order mass transfer coefficient was applied, initially the phage tracers were considered to be conservative, experiencing no sorption or decay. An immobile (Chalk matrix) porosity of 38% was assigned to the entire model domain, consistent with literature data for the Lewes and Seaford Chalks (see Chapter 3) and the value adopted by Buckle (2005).

Longitudinal dispersivity (α_x) was initially taken as 25m derived from the tracer test analysis; transverse and vertical dispersivity were adopted on a constant ratio of α_x:α_y:α_z 1:0.1:0.01 applied globally to the entire model domain.

Tracer injection concentration equal to the tracer sources was represented as an initial point source concentration at the location of each injection and the model run for a period of 60 days to simulate tracer breakthrough at observation points. Analytical modelling of the tracer test breakthroughs in section 6.2 provided an estimate of initial dispersivity and mass transfer coefficient parameters for the karst system which were applied to the entire geometry. Calibration explored the sensitivity of the model to changes in these transport parameters, within the range determined by the tracer testing and the simulation effectiveness was measured by visual fit to the data and by calculation of square residuals and root mean square error against observations. A summary of the calibration steps is presented in table 7.8, the simulated tracers concentrations versus time at receptors are presented in Figures 7.19, 7.21 and 7.20.

Model revisions 1-12 simulated only the transport of *Serratia Marcescens* phage from Water End to observation points. The timing, pattern and magnitude of breakthroughs can be reasonably well replicated by the modelling and the actual concentrations observed are within similar range to that observed at all locations, except for the peak concentrations at Arkley Hole and Lynchmill Spring which are both underestimated.

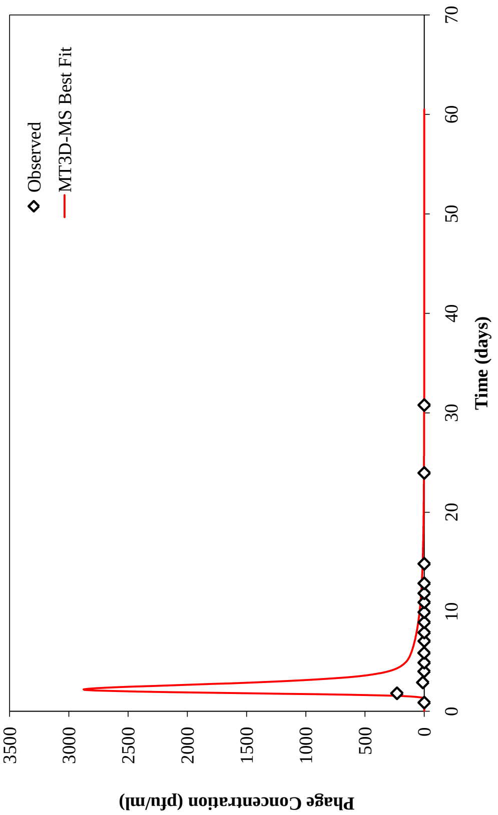
To investigate if the underestimation might be due to inadequacy of the flow model boundary conditions to simulate spring discharge rather than the transport model, the drain cells at Arkley Hole and Lynchmill Spring were simulated with a 5m lower drain elevation (Revision 5) and with the drain cells removed and replaced with wells with abstractions equal to the average long term discharge of both springs (6Ml/day at Arkley Hole, 4Ml day at Lynchmill Spring), but neither alternative representation resulted in improvement of simulated peak concentrations and the modifications were removed.

Model revisions 13-19 apply additional point source concentrations to simulate the Harefield House ($MS2$ phage) and Comet Way ($\Phi X174$ phage) tracer injections, initially using the same parameterisation as for the Water End karst system. The initial attempt was able to reproduce the time and distribution of breakthrough from Comet way approximately, including the bypass of Hatfield PWS, consistent with the karst conduits inferred position on the margins of the main karst zone. However, the magnitude of breakthroughs of $\Phi X174$ phage from Comet Way are not well reproduced, being higher than actually observed and simulations have a long tail that increases to a secondary peak towards the end of the tracer testing, possibly representing the majority of the breakthrough via slower flowpaths.

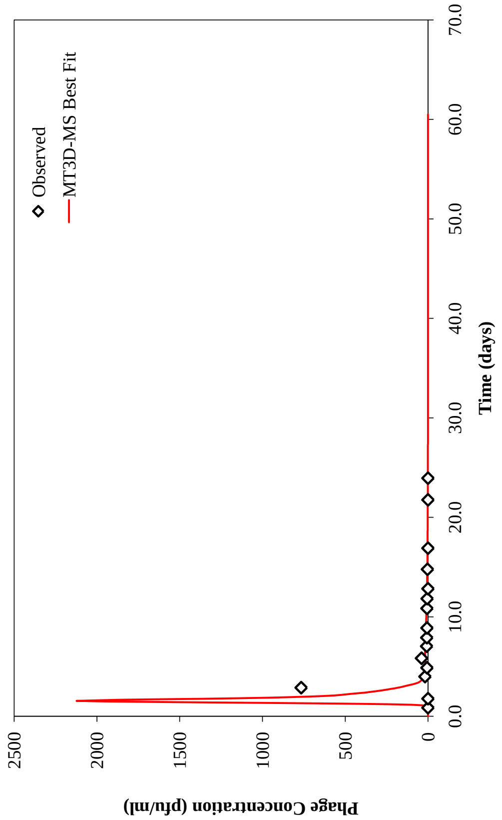
A possible cause of the discrepancy is the method used to simulate the tracer source term, which has been defined as a point source initial concentration equal to the injected mass which is diluted under conditions imposed by the recharge boundary condition. Sampling of the injection boreholes indicated that the release of tracer to the aquifer was not instant or uniform and probably occurred as an exponentially decaying release similar to that a borehole dilution test. The initial modelling has also assumed the phage tracers to be conservative, when in fact some inactivation and/or sorption of the bacteriophage will have occurred. These pro-

Table 7.8: Summary of calibration changes made to the transport models for the tracer test simulation

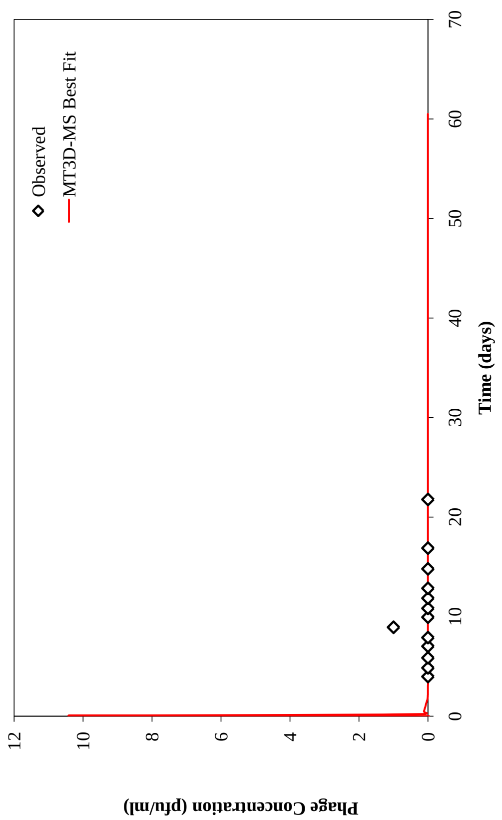
Model Run	Effective Porosity (%)	Longitudinal Dispersivity (α_x) (m)	Mass Transfer Coefficient (ω)	Comments
Initial	0.007	25	2×10^{-5}	Timing of breakthrough is too early. Peak concentrations are generally underestimated. Form of tailing, including some secondary peaks is generally well replicated
Rev 1	0.008	10	2×10^{-5}	Timing of breakthrough improved but still slightly fast. Tailing reasonable but slightly too dispersed at some locations. Peak concentrations at springs improved but still underestimated
Rev 2	0.008	10	5×10^{-5}	Peak concentrations underestimated
Rev 3	0.008	10	5×10^{-6}	Closer fit to peak concentrations. Dispersion and tailing too wide
Rev 4	0.007	25	5×10^{-7}	Dispersion and tailing too wide
Rev 5	0.007	10	5×10^{-5}	Spring Peak concentrations underestimated. Timing of breakthrough too early
Rev 6	0.007	10	5×10^{-6}	Spring peak concentrations increased at expense of tailing and greater dispersion
Rev 7	0.007	0	5×10^{-5}	No mechanical dispersion, narrowed peaks and reduced peak concentrations, some dispersion still occurs as a result of numerical solution/dual domain exchange
Rev 8	0.008	50	1×10^{-5}	Only slightly increased peak dispersion
Rev 9	0.008	10	1×10^{-5}	Narrowed peak, better capture of tailing
Rev 10	0.008	10	none	No Dual porosity, low peak concentrations
Rev 11	0.008	10	5×10^{-5}	Arkley Hole and Lynchmill Spring replaced with well boundaries Negligible effect on modelled concentrations
Rev 12	0.009	10	1×10^-5	Breakthrough occurs too late
Rev 13	0.008	10	5×10^{-6}	Reasonable replication of timing from Comet Way. $\Phi X174$ Concentrations too high. No breakthrough from Harefield House
Rev 14	0.008	25	5×10^{-6}	Decay added (see main text)
Rev 15	0.008	25	5×10^{-6}	Added extended karst zone to Vale of St Albans
Rev 16	0.008	25	5×10^{-6}	Changes to decay constants for $\Phi X174$ and $MS2$ result in an improved fit
Rev 17	0.008	25	5×10^{-6}	Added decay to *Serratia Marcescens* phage
Rev 18	0.008	25	1×10^{-5}	
Rev 19	0.008	25	1×10^{-6}	Increased hydraulic conductivity of karst extension to 75m/d



(a) Hatfield PWS

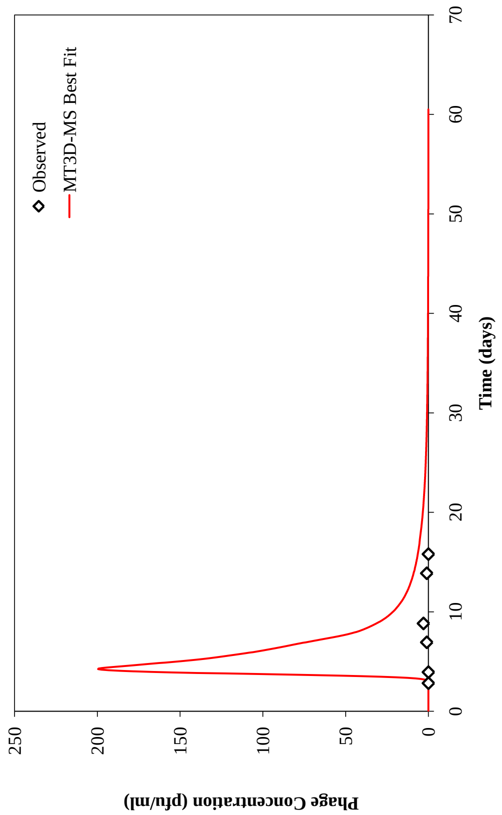


(b) Essendon PWS

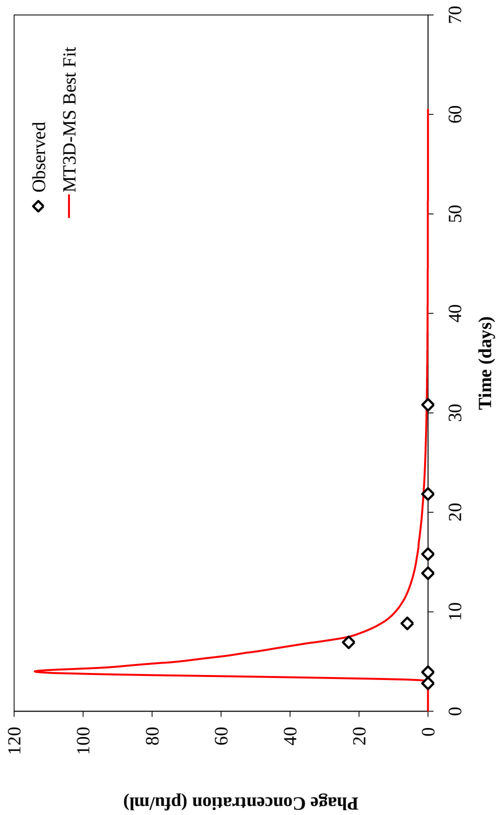


(c) North Mymms PWS

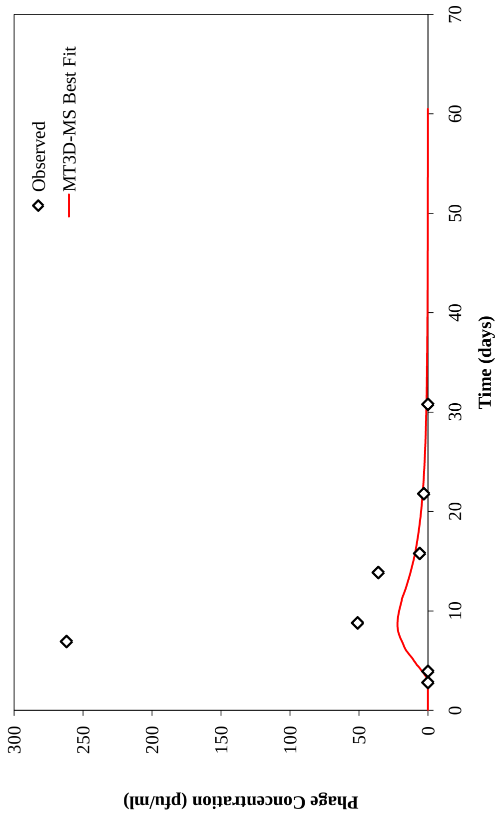
Figure 7.19: Simulations of the *Serratia Marcescens* tracer breakthrough from Water End at Hatfield PWS, Essendon PWS and North Mymms PWS



(a) Rye Common PWS

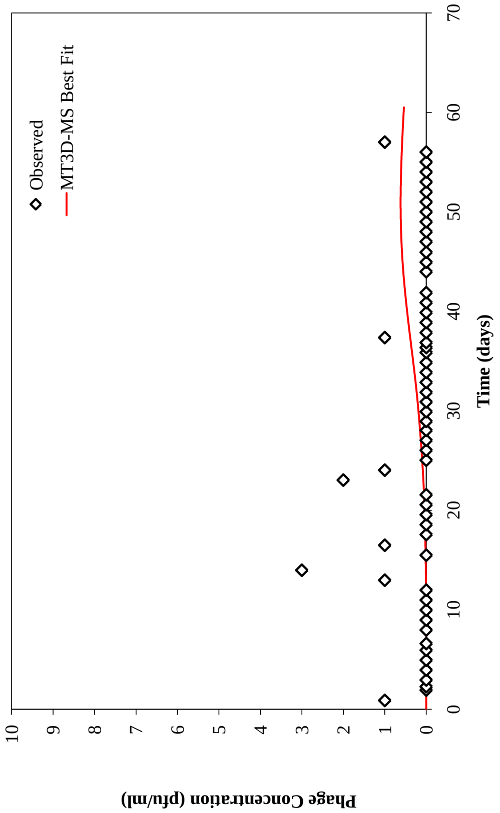


(b) Amwell Marsh PWS

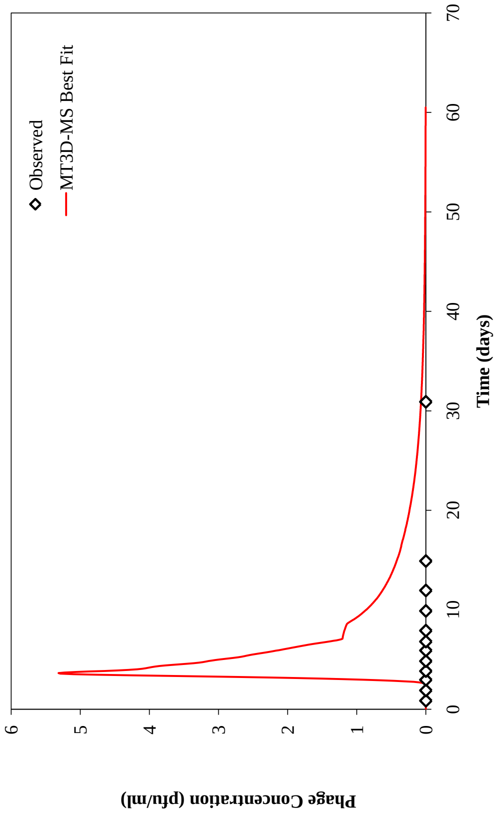


(c) Turnford PWS

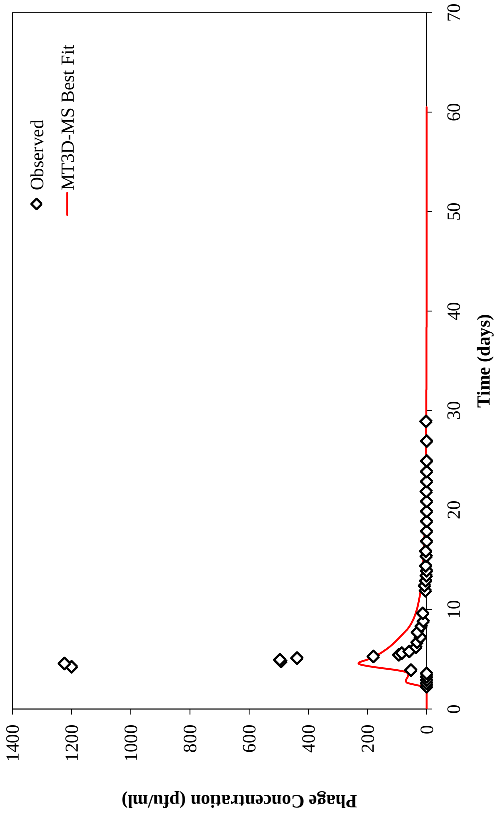
Figure 7.20: Simulations of the *Serratia Marcescens* tracer breakthrough from Water End at TWUL Abstraction Wells



(a) Arkley Hole



(b) Chadwell Spring



(c) Lynchmill Spring

Figure 7.21: Simulations of the *Serratia Marcescens* tracer breakthrough from Water End at springs

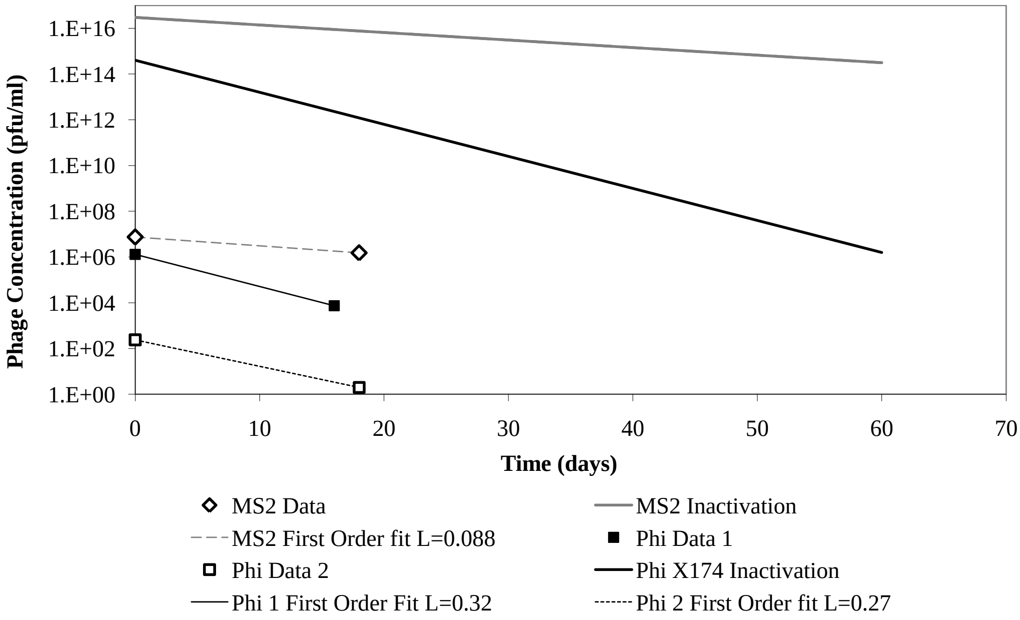


Figure 7.22: Fitting of first order decay model to phage concentrations in injection boreholes and idealised literature inactivation rates, L=Λ

cesses are difficult to quantify a-priori in a groundwater flow model especially since they are likely to be complicated by two region mass transfer processes (both dual porosity diffusive and stagnant zones).

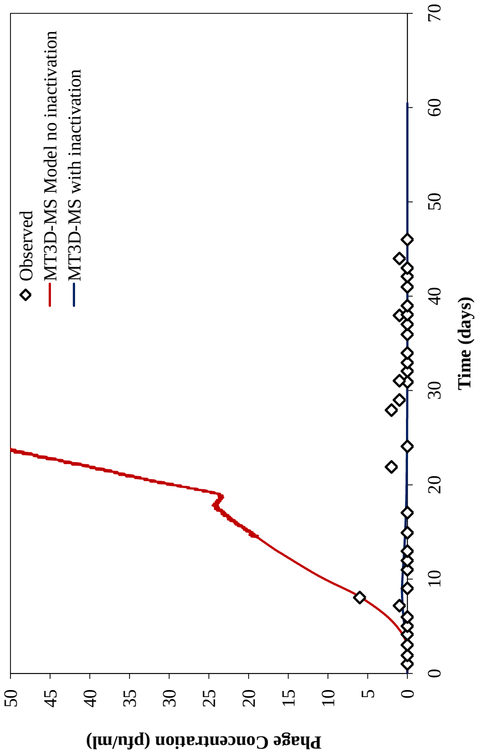
MT3D-MS does allow for alternative representations of the tracer source. One possibility would be to model the release as an injection well with known discharge and concentration, or as mass flux boundary. This would require detailed knowledge of the actual tracer flux which unfortunately is not available since monitoring of the injection boreholes suggested poor mixing.

A simpler approximation of both inactivation and the source term was adopted. Mass balance (Section 5.6) suggests that much ($\geq$ 99.9%) of the injected mass left the borehole quickly. Therefore decline in the residual borehole mass is probably a result of inactivation. To derive inactivation rates (see figure 7.22) a first order model was fitted and compared with literature derived rate constants (0.075day^{-1} for $MS2$ phage and 0.32day^{-1} for $\Phi X174$).

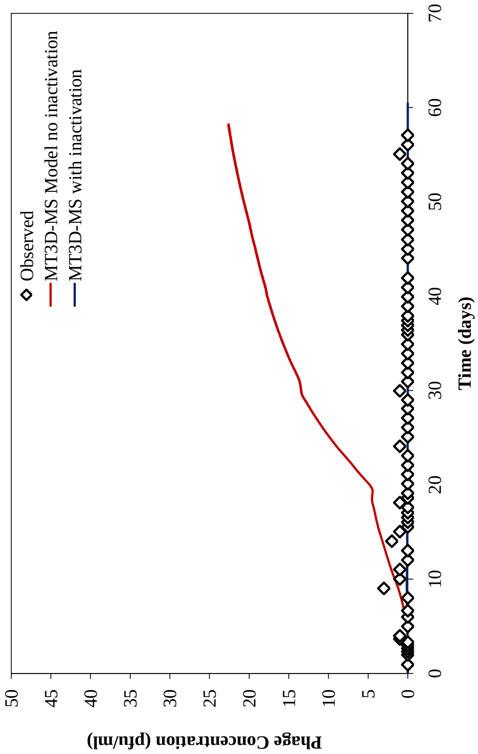
Fitting of rate constants suggest a value of 0.088day^{-1} for $MS2$ phage and $0.27 - 0.323$day^{-1} for $\Phi X174$. These are probably slight over-estimates because it is assumed any advective loss has been ignored.

Simulated breakthroughs of $\Phi X174$ incorporating a first order decay ($\lambda = 0.3$) are presented in Figure 7.23. The addition of first order decay improves the fit of simulated breakthroughs to observed data with Essendon PWS, Arkley Hole and Lynchmill Spring showing higher concentrations than other locations.

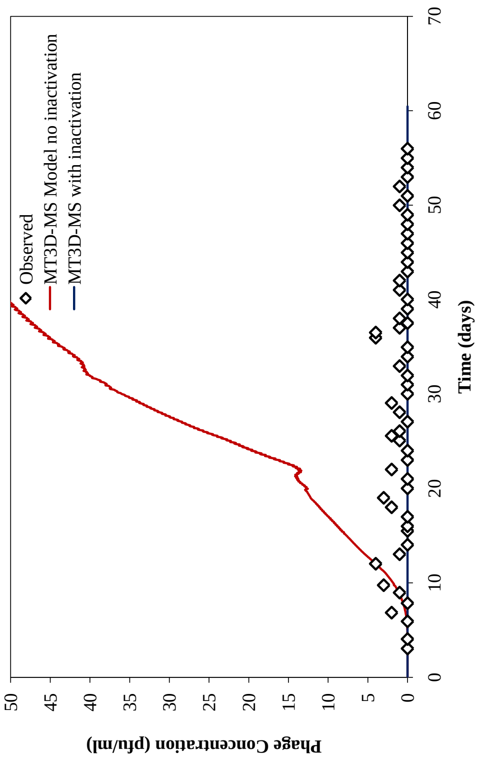
A improved fit to the observed data can be achieved either by reducing the mass transfer coefficient or by slightly reducing the decay constant (Revision 16), or changing both in combination (Revision 17) resulting in a good fit to observed



(a) Essendon PWS



(b) Arkley Hole Spring



(c) Lynchmill Spring

Figure 7.23: Initial simulated breakthroughs of $\Phi X174$ tracer at Essendon PWS, Arkley Hole Spring and Lynchmill Spring with (Revision 14) and without (Revision 13) first order decay/inactivation

data. The calibrated plots at observation points are presented in Figures 7.24 and 7.25.

In the initial simulations, breakthrough of $MS2$ phage from Harefield house only occurred at Nashes Farm, where as for the initial $\Phi X174$ simulations, concentrations were higher than observed. The lack of a simulated breakthrough of $MS2$ phage from Harefield house unsurprising given the parameterisation of the model - the model contains no explicit representation of the karst inferred from the tracer test results in the Vale of St Albans.

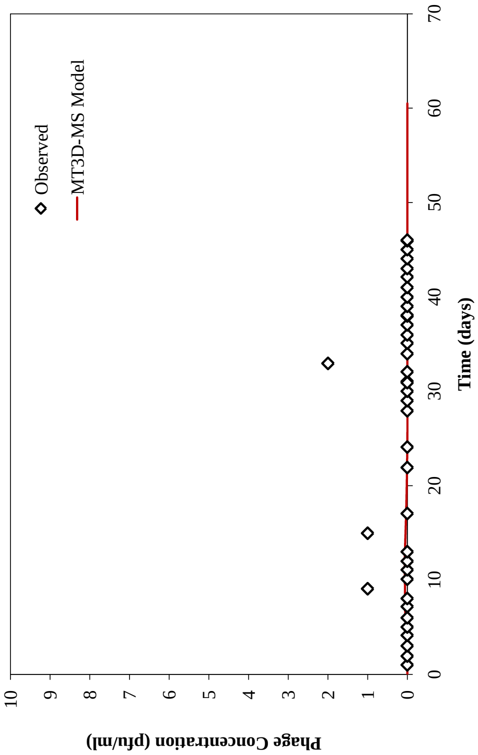
To simulate the occurrence of karst flows within the Vale of St Albans, an extension was added to the main karst zone extending in a WNW direction across the Vale of St Albans from approximately the position of Comet Way to the Harefield house borehole. This zone, approximately 200m (one model grid cell wide), is indicated in Figure 7.26. It has been defined on the basis of the tracer test results and the conceptual understanding that relict karst may exist within the Vale. Since there is no apparent surface karst by which to constrain its position, it has been located along the approximate centre line of the bromate plume and the approximate L1 geomorphological lineation of Bloomfield et al. (2005) extending along the dry valley northwest of Sandridge.

The inclusion of an extended element of karst into the Vale of St Albans resulted in improved simulation of the breakthrough of $MS2$ phage from Harefield House and the initial estimate of effective porosity resulted in approximately correct breakthrough times however, as with the $\Phi X174$, simulations the magnitude of the breakthroughs were over-estimated. The addition of a first order decay term consistent with the literature and field data ($\lambda = 0.0815$) resulted in an improved representation. Further increasing λ to a value of $0.1 day^{-1}$ and increasing hydraulic conductivity to $75 m/day$ resulted in a good fit to the pattern of observed data and is simulated breakthrough curves are presented in Figures 7.27 and 7.28.

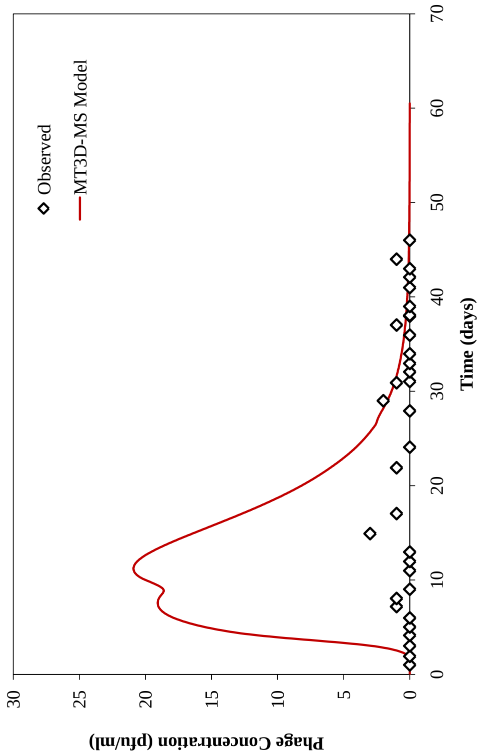
7.5 Summary

Close representation of all three tracer breakthroughs has been achieved using a single set of transport parameters for the Hertfordshire karst. The final calibrated parameters (Table 7.9) provide the best visual fit to observed data, at all locations, for all tracers. These parameters do not necessarily give the best statistical fit (which is biased towards the more frequent observations of the tailing) but they capture peak concentrations and the relative timing and tailing of breakthroughs. They are also consistent with the estimated range of parameters for the karst system derived from analytical modelling of tracer breakthrough curves, and the modelled decay rates agree closely with literature data for bacteriophage (e.g. Gerba et al., 1991).

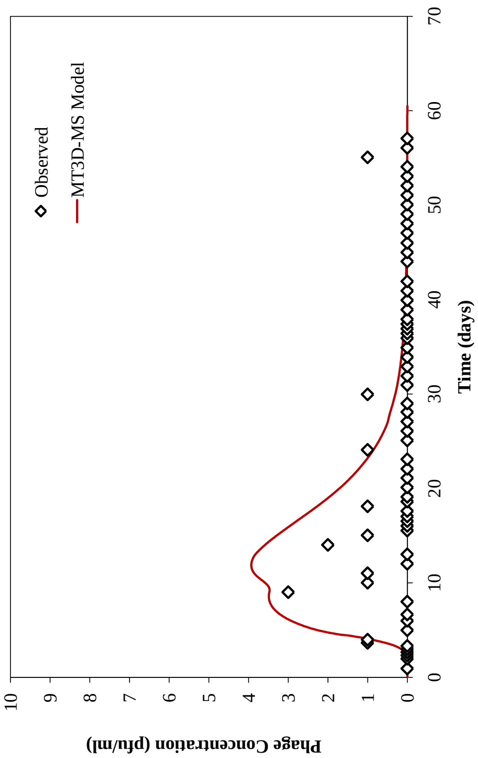
The calibrated parameters represent the best approximation of all observed



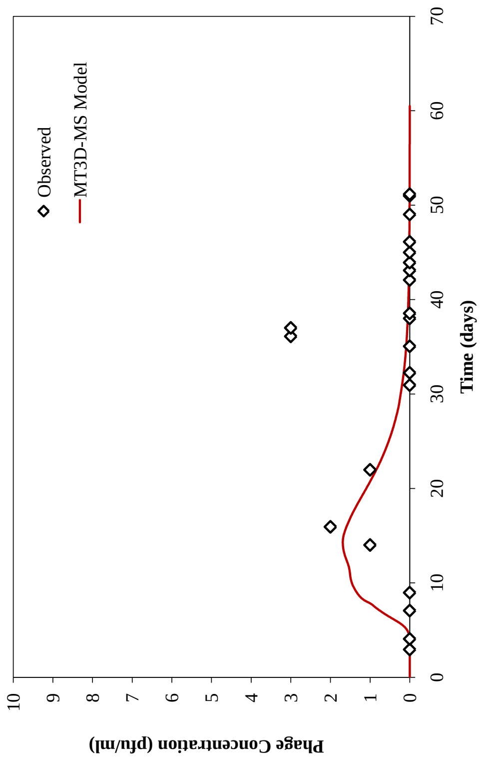
(a) Hatfield PWS



(b) Essendon PWS

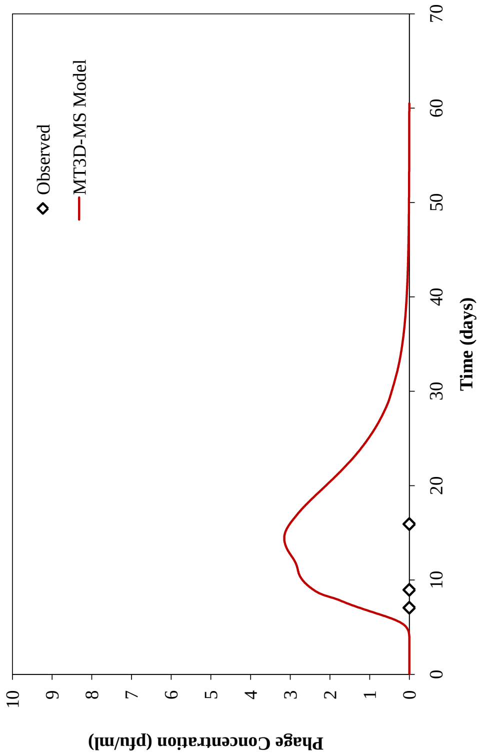


(c) Arkley Hole

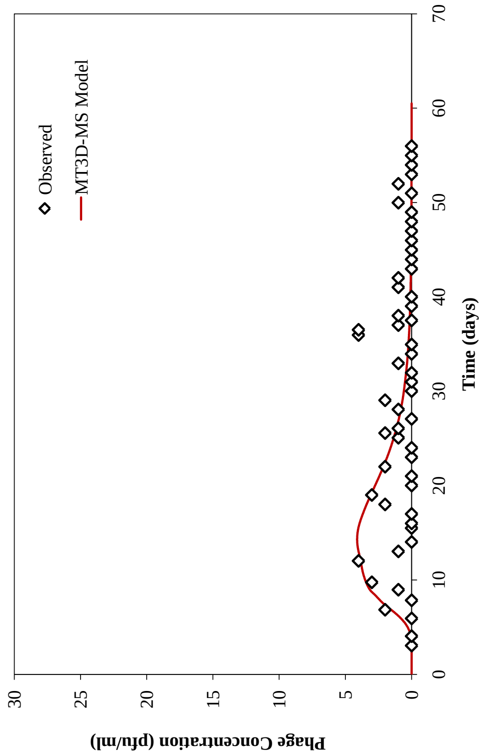


(d) Amwell Marsh PWS

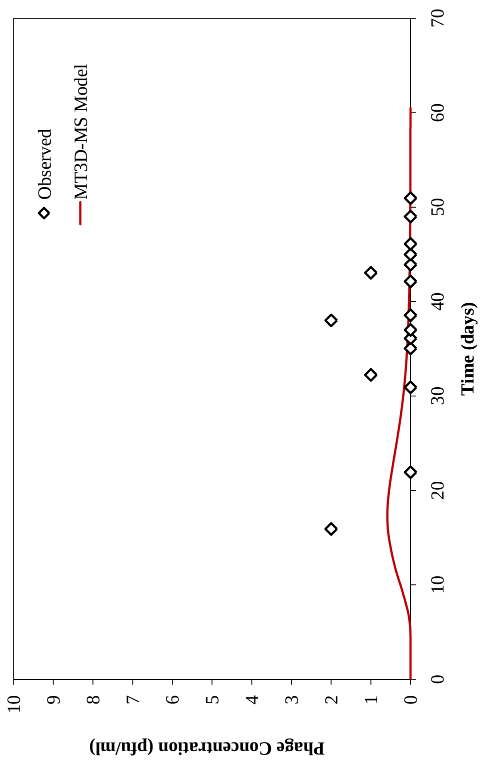
Figure 7.24: Simulations of the $\Phi X174$ tracer breakthrough from Comet Way, Hatfield at observation points between Hatfield and the Northern Lee Valley.



(a) Rye Common PWS



(b) Lynchmill Spring



(c) Turnford PWS

Figure 7.25: Simulations of the $\Phi X174$ tracer breakthrough from Comet Way, Hatfield at observation points in the central and southern Lee Valley.

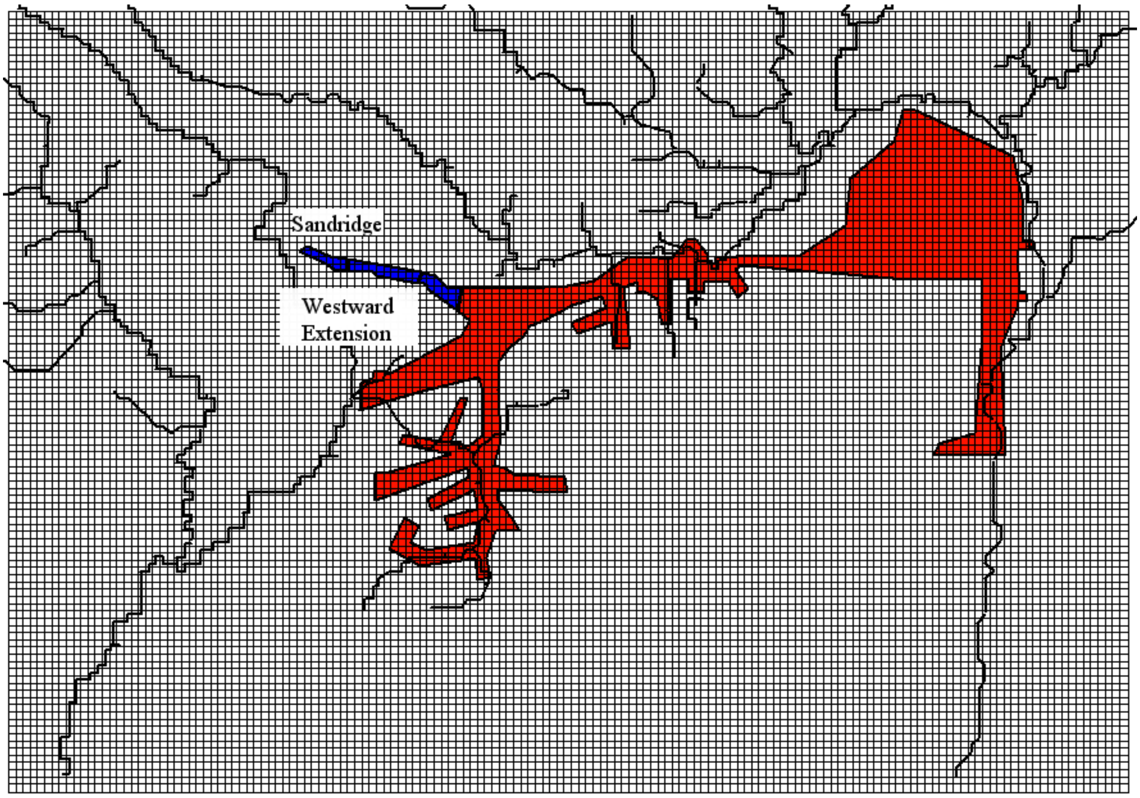
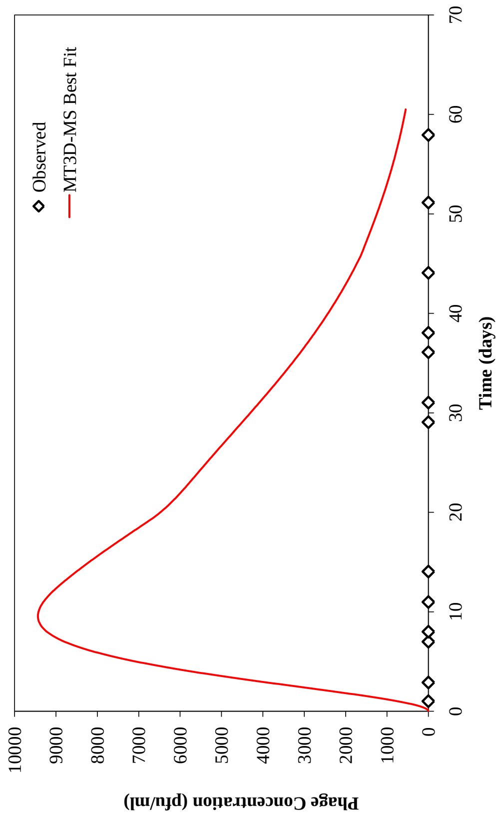


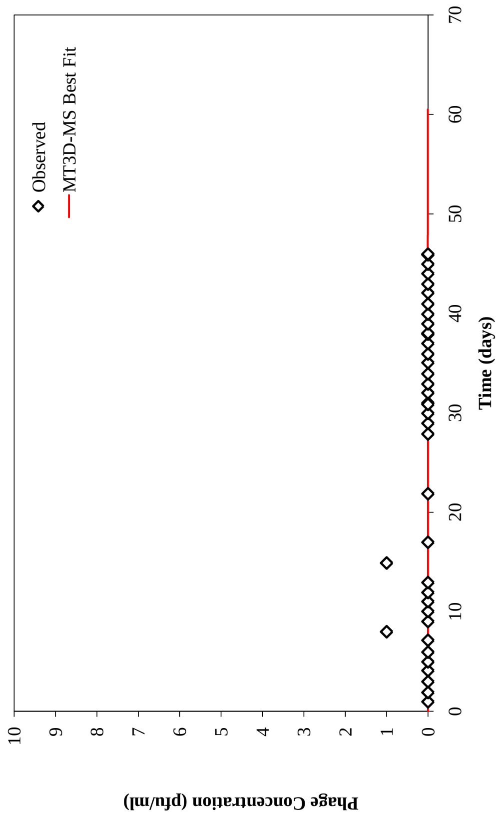
Figure 7.26: Extension of the modelled karst geometry into the Vale of St Albans, the extension zone has been assigned the same transport parameters as the main zone, a hydraulic conductivity of 50m/day was initially assigned, that same as that to the marginal karst zone in the vicinity of Hatfield

Table 7.9: Final calibrated parameter set for the EPM Hertfordshire karst model simulation of tracer breakthroughs

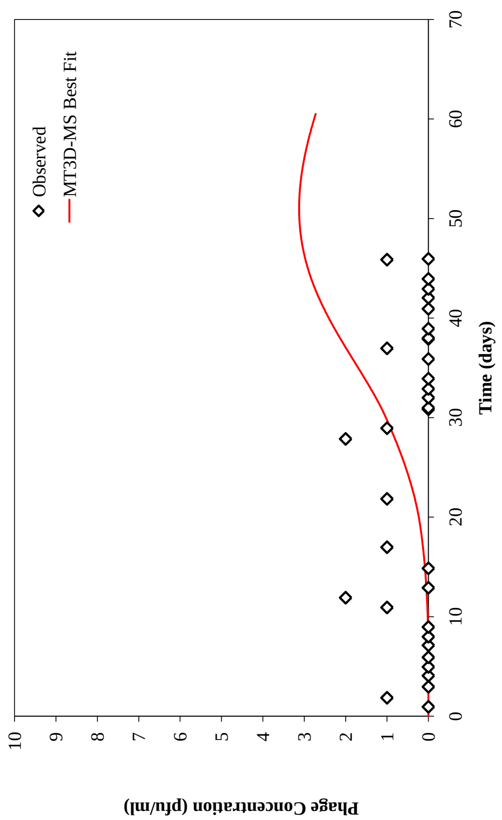
	Effective Porosity (%)	Immobile Porosity (%)	Mass Transfer Coefficient (ω)	Dispersivity $\alpha_x : \alpha_y : \alpha_z$ (m)	Decay Constant day^{-1}
General	0.008	38	1×10^{-6}	25:2.5:0.25	-
Serratia Marcescens					0.1
$\Phi X174$					0.2
$MS2$					0.1



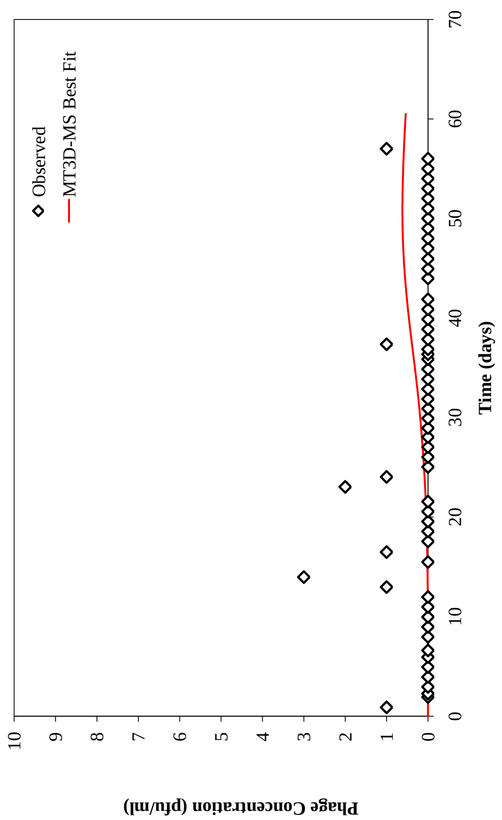
(a) Nashes Farm



(b) Hatfield PWS

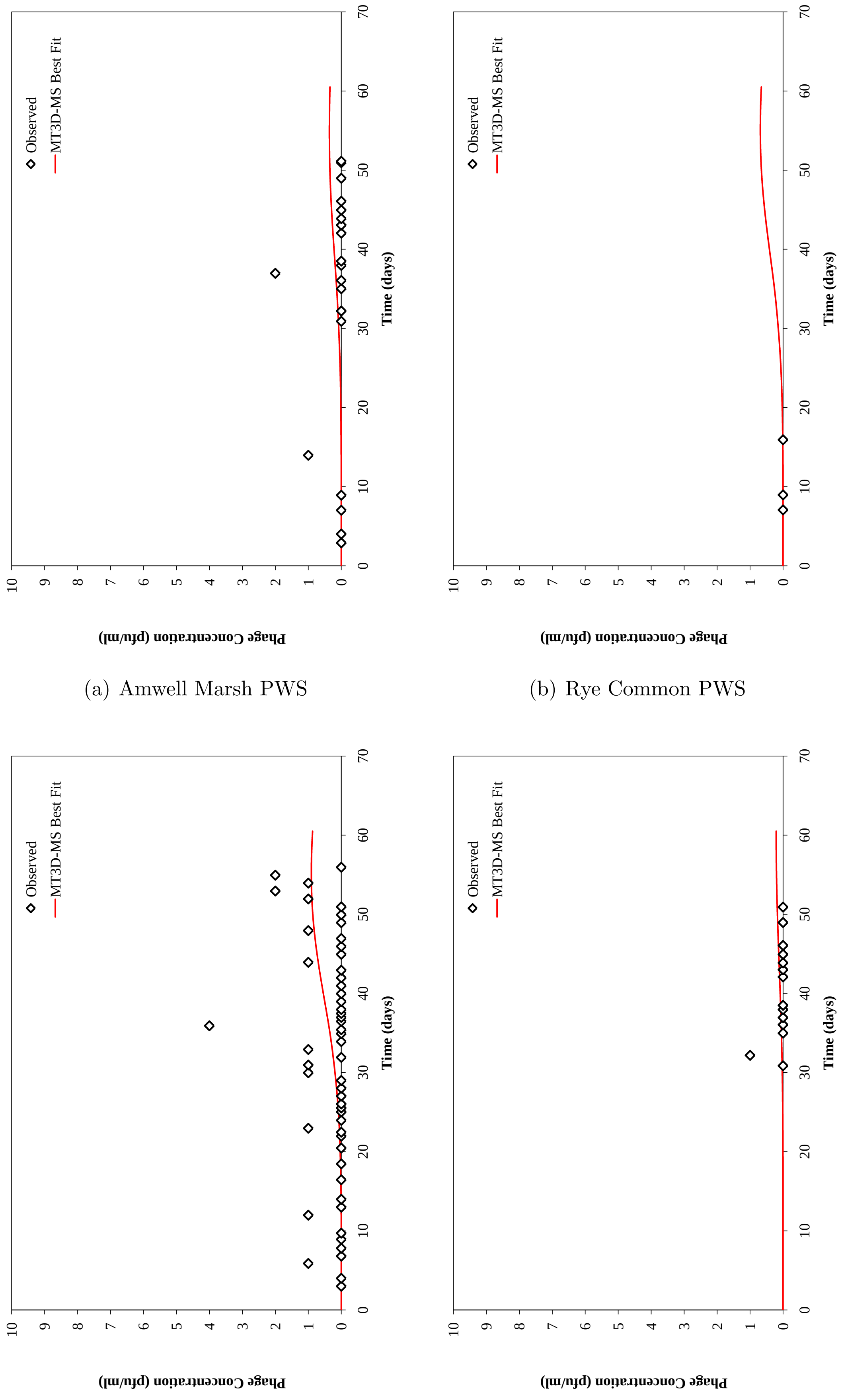


(c) Essendon PWS



(d) Arkley Hole

Figure 7.27: Simulations of the $MS2$ tracer breakthrough from Harefield House, Sandridge to Nashes Farm, Hatfield PWS, Essendon PWS and Arkley Hole Spring . Note the high concentration breakthrough at Nashes farm which was not observed in the tracing, this highlights a limitation of the Equivalent Porous Media approach in representing heterogeneous fractured aquifers, see text for further discussion



(a) Amwell Marsh PWS

(b) Rye Common PWS

(c) Lynchmill Spring

(d) Turnford PWS

Figure 7.28: Simulations of the $MS2$ tracer breakthrough from Harefield House, Sandridge at abstraction wells and springs in the Lee Valley

breakthroughs using the EPM representation of the karst system. It is apparent that the single parameter set does not work equally well for all locations or breakthroughs. For example, at springs a better fit can be obtained by reducing dispersivity and dual domain exchange at the expense of additional tailing elsewhere. Localised calibration is not however justified by available data. Localised calibration is also difficult to justify within an EPM representation which can only ever provide an approximation of highly discrete features.

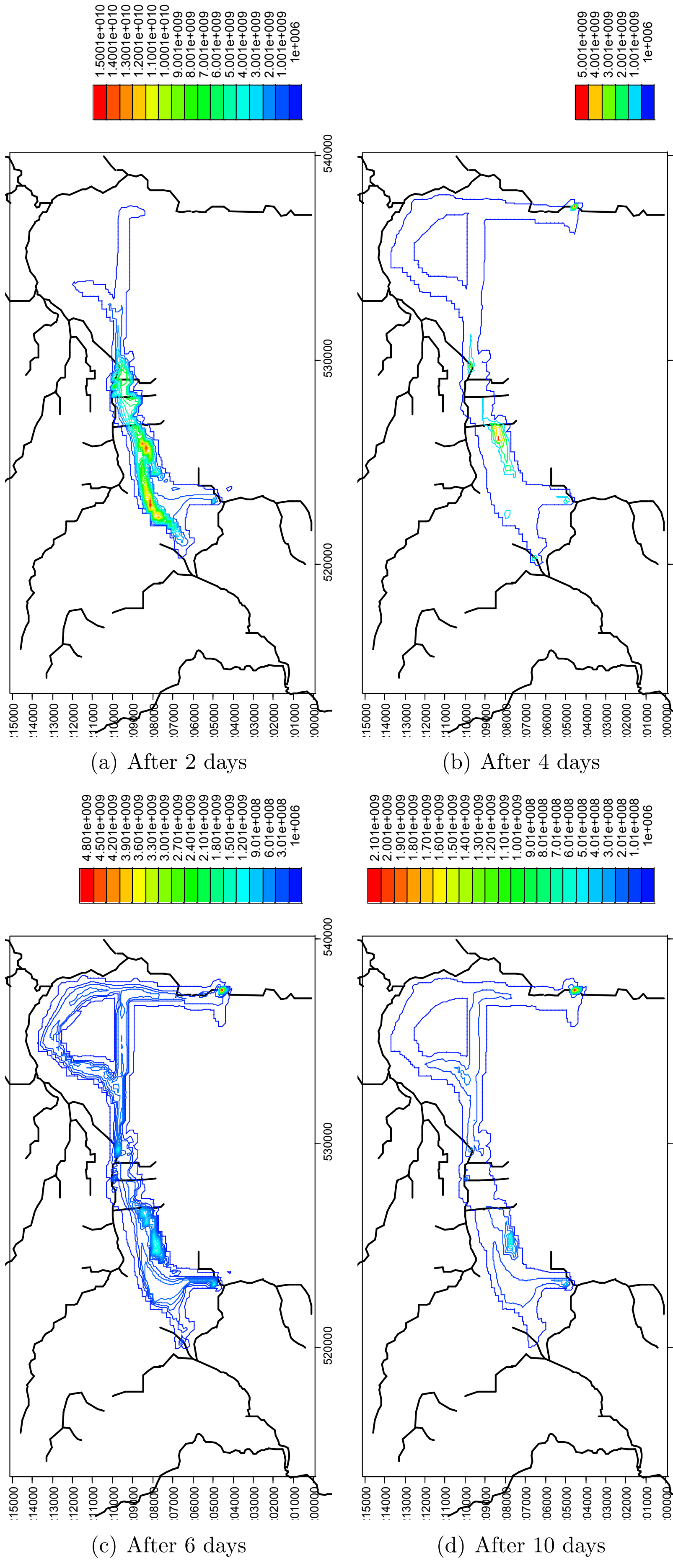
The spatial distributions of the simulated tracer migration presented in Figures 7.29, 7.30, 7.31 and 7.32 indicate that the bulk of tracer has moved along the defined karst zone approximately coincident with the Palaeocene feather edge.

In addition to simulating observed tracer behaviour, the modelling exercise has also replicated or indicated additional characteristics of the 2008tracer test:

- The low concentration < 5pfu/ml breakthrough simulated at Chadwell Spring is close to the phage detection limit and it is therefore possible that a connection was simply missed by the intermittent sampling at Chadwell Spring.
- It is simulated that breakthrough of tracer occurred at Hoddesdon PWS and Broxbourne PWS which were not monitored
- The simulations of transport from Comet Way and Harefield House both indicate a bypass of Hatfield PWS
- Simulations of tracer from Comet Way indicate low level, near-detection breakthroughs might have occurred at Amwell Marsh PWS and also could have Rye Common PWS.
- Tracer sampling may have terminated too early to detect measurable concentrations of tracer from Harefield House at Amwell Marsh, Rye Common and Turnford PWS at Amwell Marsh, Rye Common and Turnford PWS

The simulated concentrations of $\Phi X174$ phage from Comet Way are close to the phage detection limit of $\geq 1pfu/ml$. The observed near background concentrations of $\Phi X174$ might be due to a relatively lower injection concentration, a non instantaneous source flux, phage inactivation and possibly sorption.

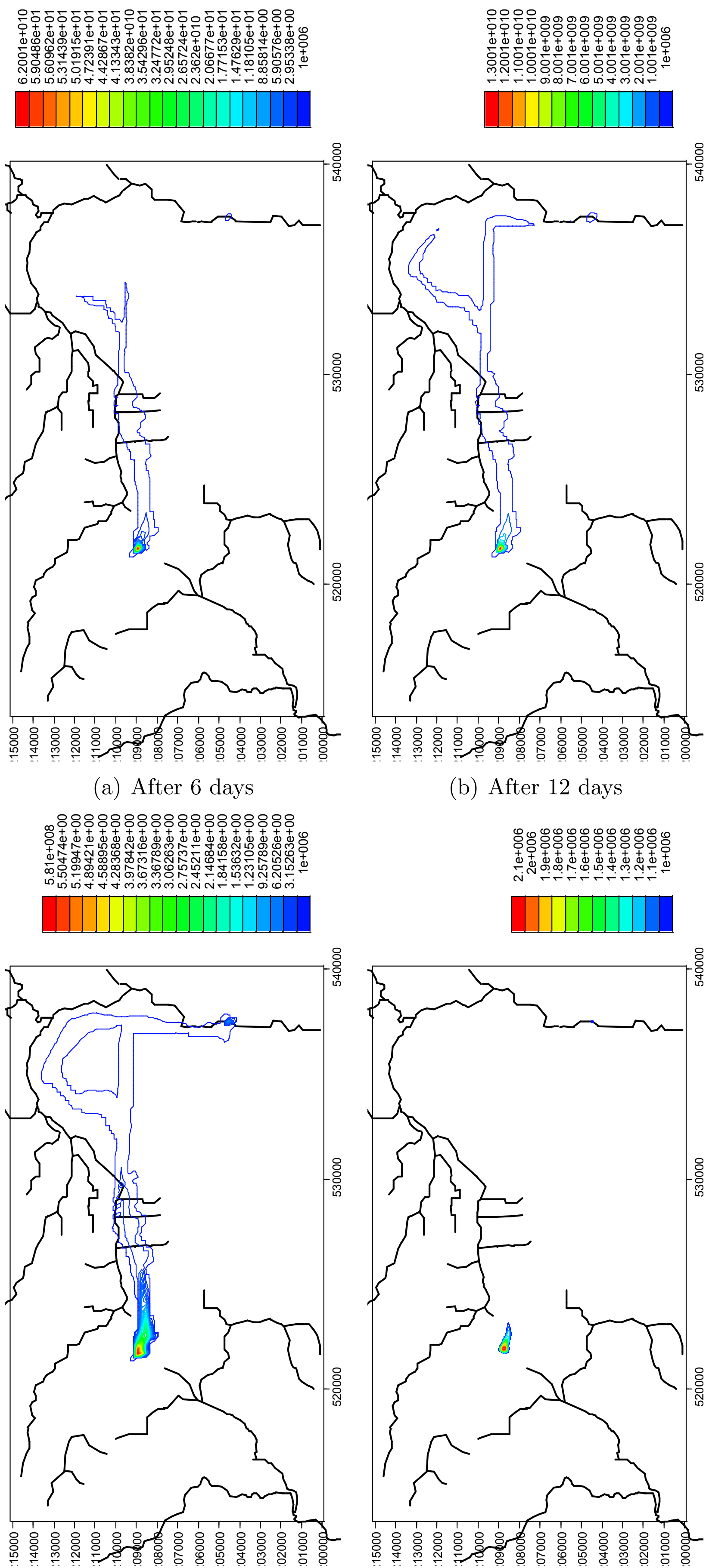
To assess sensitivity of *Serratia Marcescens* phage to inactivation, during the tracer test it was simulated with a decay constant of 0.1 day^{-1} (Model Revision 17) which the effect of slightly reducing overall peak concentrations but does improved model representation at long times. Decay of *Serratia Marcesens* does not appear to be an important factor, however due to the slightly improved fit and more realistic representation the decay has been retained. Field data suggest that survival of *Serratia Marcescens* is similar to, or better than $MS2$, reflecting the data of (Skilton and Wheeler, 1989).



(a) After 2 days (b) After 4 days

(c) After 6 days (d) After 10 days

Figure 7.29: MT3D-MS spatial distributions of a simulated *Serratia Marcescens* phage injection at Water End. Model Concentrations are given as pfu/m^3 (1pfu/m^3 = 1×10^{-6}pfu/ml)



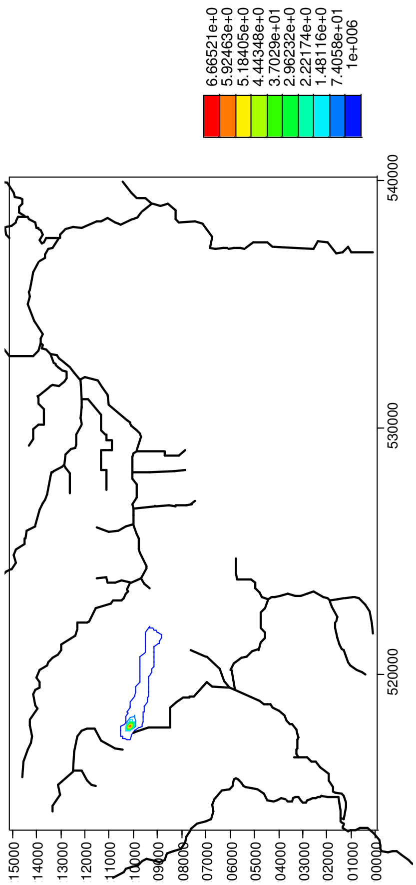
(a) After 6 days

(b) After 12 days

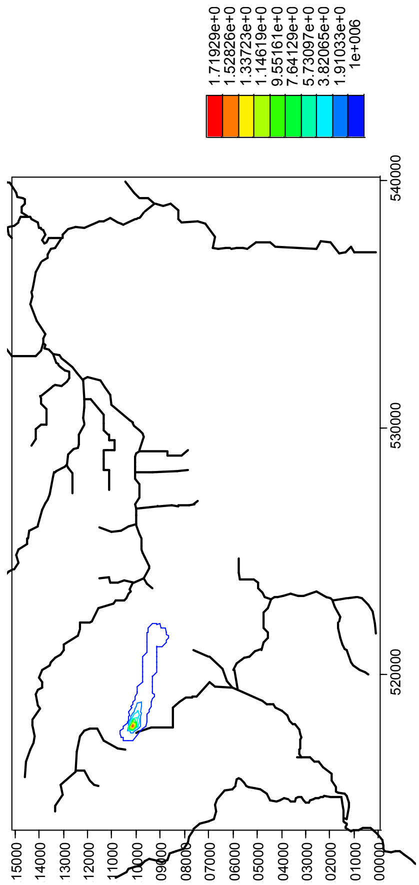
(c) After 24 days

(d) After 50days

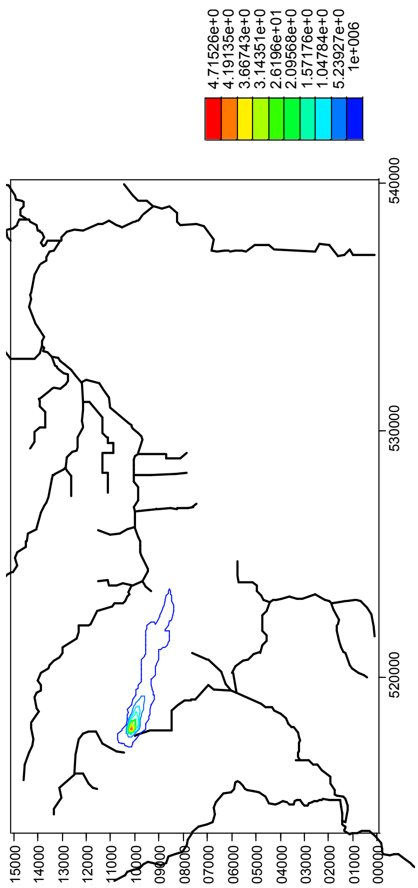
Figure 7.30: MT3D-MS spatial distributions of a simulated $\Phi X174$ phage injection at Comet Way. Model Concentrations are given as pfu/m^3



(a) After 10 days

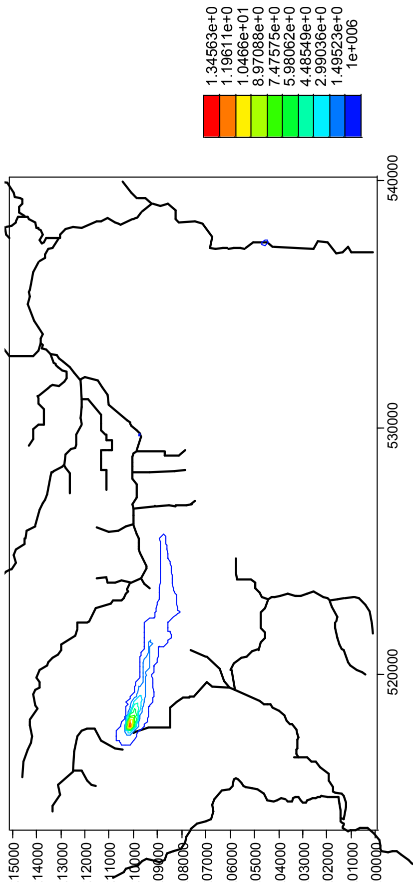


(b) After 20 days

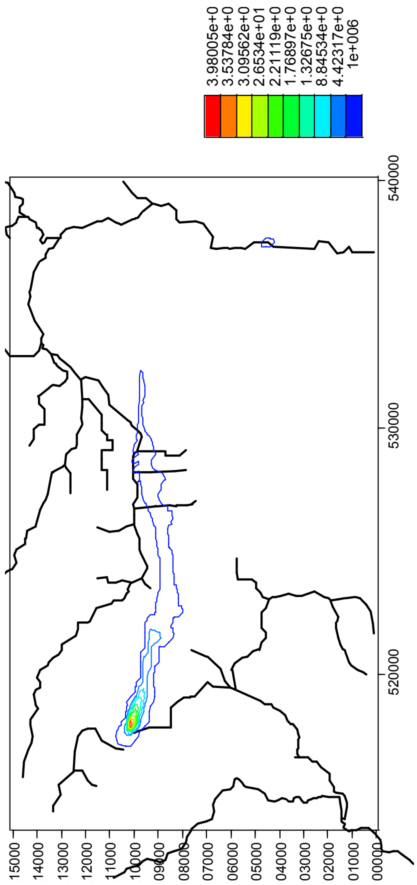


(c) After 30days

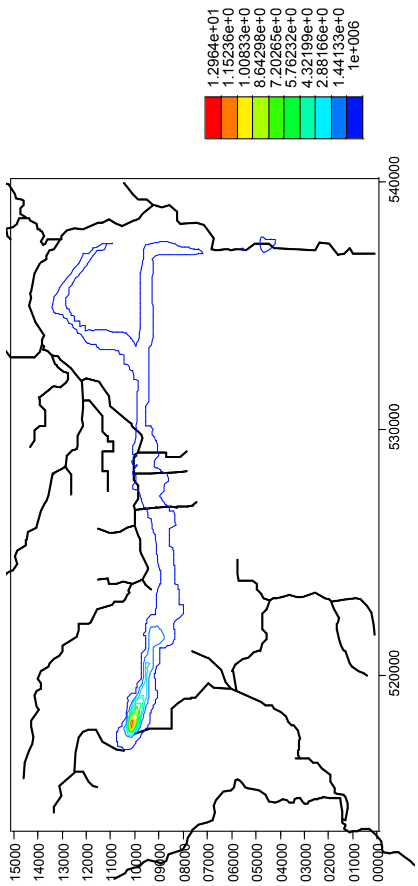
Figure 7.31: MT3D-MS spatial distributions of a simulated $MS2$ phage injection at Harefield House. Model Concentrations are given as pfu/m^3



(a) After 40 days



(b) After 50 days



(c) After 60 days

Figure 7.32: MT3D-MS spatial distributions of a simulated $MS2$ phage injection at Harefield House. Model Concentrations are given as pfu/m^3.

The spatial distribution of simulated tracer concentrations also highlights the principal limitation of an EPM representation of transport in discrete fractures and conduits. Locations within or adjacent to the modelled karst geometry where tracer was not detected (e.g. Nashes Farm on Figure 7.31, Park Street OBH and North Mymms PWS) do contain simulated concentrations of tracer and in the case of Nashes Farm a simulated breakthrough. This is a result of embedding the karst network into a model domain of a porous medium, which allows advective and dispersive flow to occur in any direction.

The modelling successfully captures the catchment-scale behaviour of the tracers but not all local-scale factors. This has implications for the modelling of bromate since it will not be possible to replicate the full characteristics of the “plume” such as the bypass of Water Hall PWS, observation points within the Vale of St Albans and the unaffected private locations within the Lee Valley.

Chapter 8

Modelling Bromate Transport

This chapter describes the application of the groundwater flow and transport model developed (Chapter 7) to the simulation of bromate transport.

8.1 Strategy

A principal objective of this research (see Section 1.2) is to provide predictions of the future evolution of bromate concentrations at points of interest in the aquifer under different possible future scenarios and stress conditions. Essential characteristics of the modelling in order to be able to provide robust predictions are therefore; 1) Validation of simulated concentrations against observation data where available, and 2) Approximate representation of the spatial distribution of bromate within the aquifer.

To meet this objective a spatially distributed groundwater flow and solute transport model has been developed consistent with the conceptual aquifer understanding described in Chapter 6 and calibrated for flow and transport against observations, including the catchment-scale tracer tests (Chapter 5). The model is capable of generating time series concentration at individual observation points within the model grid in addition to simulation of the spatial distribution of bromate.

Fourteen observation points (Figure 8.1) were included in the model to derive simulated bromate time series. These comprise

- One near source observation borehole at Nashes Farm
- Three spring locations at Arkley Hole, Lynchmill Spring and Chadwell Spring
- Ten major public supply abstraction wells.

8.1.1 Representation of the Bromate Source

The NNR groundwater flow and transport model had a simple representation of Bromate release comprising a specified concentration point source of $5000\mu g/l$ located

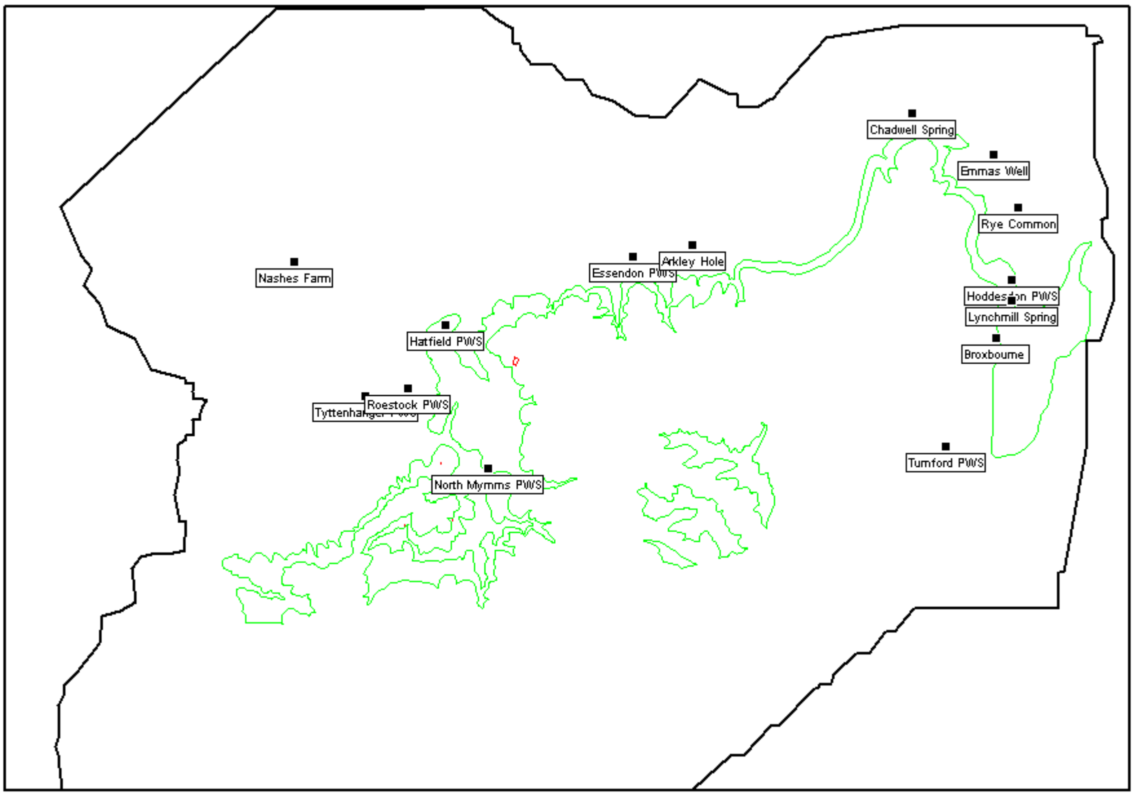


Figure 8.1: Distribution of observation points in the MT3D-MS simulations

at the position of the Sandridge site and constant for the entire model duration (Buckle, 2005). This is a Dirichlet (first type) boundary condition where the specified concentration is maintained at the boundary cell for the duration of the model and the solute is allowed to advect and or disperse into the surrounding model cells.

Selection of this boundary condition by Buckle (2005) reflected the uncertainties associated with the site history and the effect this may have had on the release of bromate into the aquifer. The constant value was adopted as it reflected on-site measurements of bromate concentrations. Sensitivity analysis of the source concentration (varying the source between $1500\mu g/l$ and $15000\mu g/l$) indicated that breakthrough at the Lee Valley could only be achieved by adopting high dispersion and/or at the expense of the spatial representation of the plume (Buckle, 2005). The $15,000\mu g/l$ source term also results in poor spatial representation of the apparent bromate "plume".

A major limitation in adopting a constant specified concentration source is that it cannot properly replicate the source history of contaminant release as a function of hydrogeological and recharge processes. It implies that the long term increase in bromate concentrations observed prior to adoption of the scavenge pumping is as a result of leading edge breakthrough of a persistent contaminant source. It also excludes alternative explanations such as changes in source flux, for example due to a catastrophic spill. Since the source is constant it cannot reduce with time, reflecting loss of mass from the source zone, and if run for long enough the model will achieve a pseudo-equilibrium. Whilst this might give estimates of the possible long term maximum concentration at receptors, this source model is highly unrealistic since it does not account for any changes at the source site.

Release of bromate into the ground beneath the site could have occurred at any point during the operation of the Sandridge chemical works between 1955 and 1980 and may have continued to occur following closure and redevelopment of the site. It is possible that release from the unsaturated zone and/or by diffusion from contaminated pore water might still be occurring beneath St Leonard's Court. Fitzpatrick (2010) has attempted to constrain the bromate release based upon available monitoring data, apparent ratios between bromate and bromide concentrations, and dual porosity modelling and concludes:

- Some bromide contamination must have occurred prior to 1983 due to its presence at high concentrations in observation boreholes downgradient of the site at that time
- Bromide and Bromate may have similar release histories, however there is some evidence to suggest release of bromide might have occurred earlier, or to a greater extent than bromate prior to 1983.
- Decline in porewater and groundwater concentrations between the late 1980's and start of frequent monitoring in 2000 is inferred to indicate a loss of mass from the site and migration away through groundwater. This may coincide with site clearance resulting in increased flushing by recharge from 1984 until housing construction began in 1987.

Based upon these, and other constraints, Fitzpatrick (2010) has developed three scenarios for bromate release representing a best, a worst and a median case. These scenarios are presented in Figure 8.2 and summarised below:

- **Scenario A** Represents a combined catastrophic release and later recharge pulse. The "catastrophic release" is modelled by assuming a mass flux equal to 1984-85, inferred from measured bromide concentrations, occurred between period 1960-1983 coupled with high concentrations as a result of a site clearance to 1987.
- **Scenario B** Represents a case where bromate and bromide share a common history of release and bromide concentrations can constrain the likely range of bromate. Input of bromate mass occurs at a low rate prior to 1984 with a high mass flux associated with the site clearance until 1987. Subsequent bromate release is at a much reduced rate.
- **Scenario C** Represents a low mass input case where the majority of bromate release occurred as a result of the 1984-1987 site clearance.

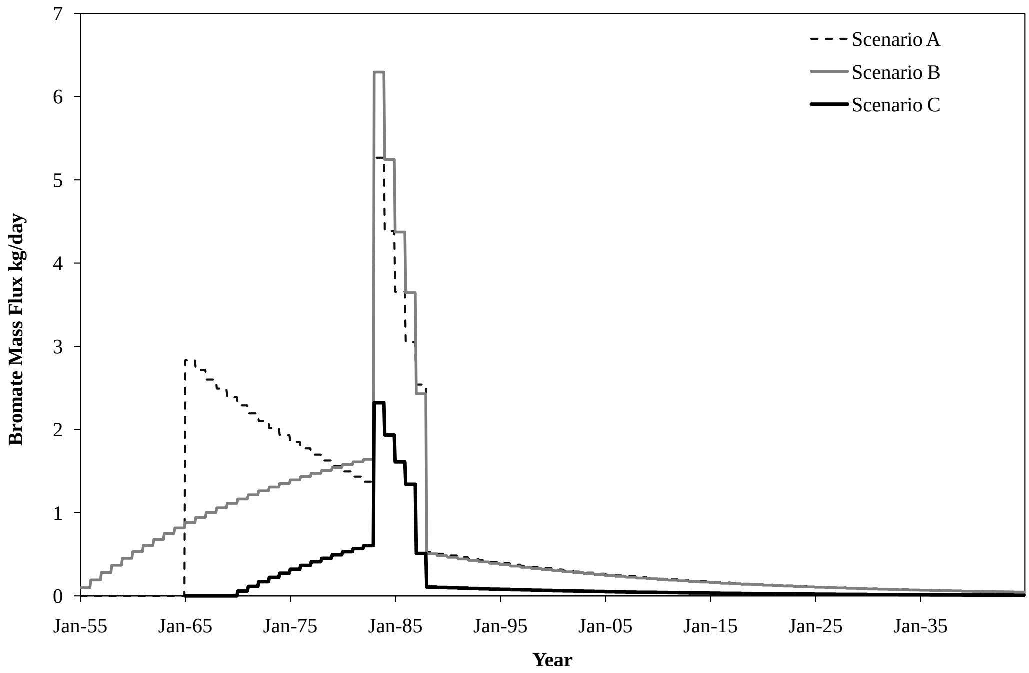


Figure 8.2: Three possible source histories for release of Bromate into the saturated zone beneath the Sandridge site. Scenario A - Worst Case, catastrophic early release and recharge pulse from 1984-1987. Scenario B - Median case comprising seepage and a recharge pulse from 1984-1987. Scenario C - Best case, recharge pulse only and late stage seepage.

These, and the 5000μg/l constant concentration (Scenario D) source term of Buckle (2005) represent four possible interpretations of the source history derived from a relatively sparse data set covering a window of more than 50 years in which bromate could have migrated from St Leonard's Court Sandridge.

These scenarios have been incorporated in model simulations as a point source specified mass flux boundary. Rather than specifying the concentration in groundwater beneath the site, the mass flux boundary adds a specified mass of a solute, in this case bromate, to the groundwater beneath site which is then mixed, diluted and transported by advective and diffusive processes. Use of this boundary condition ensures that the model mass balance is consistent with the bromate release scenarios and is independent of the flow within the source cell (Zheng and Wang, 1999).

8.1.2 Scavenge Pumping

Scavenge pumping at Hatfield PWS has proven an effective measure to limit bromate concentrations at downgradient locations and is an important process to incorporate into any predictive modelling. Two possible scenarios for future abstractions at Hatfield PWS are considered:

- Hatfield PWS continues operation as a long term scavenge pumping borehole at a rate of 6Ml/day during the winter and spring months (November to May) and 8Ml/day during summer months (June-October) for the duration of the simulation, continuing current operations.

- Hatfield PWS ceases operation.

An alternative approach to scavenge pumping at Hatfield PWS is development of a new scavenge pumping well closer to the contaminant source where bromate is less dispersed and scavenge pumping may be able to remove a greater mass per unit volume of water abstracted. The capture zone of a well in a uniform flow field is illustrated in Figure 8.3.

Assuming a uniform flow field for the Sandridge area, which is probably a reasonable approximation for the interfluve piezometery to the north west of the Vale of St Albans (Section 3.6) the width of a well capture zone is given by Q/Q_0 (Bear, 1972) (Figure 8.3) where Q is abstraction at the well and Q_0 is the regional flow. Since $Q_0 = kbi$ (Haitjema, 2006) where k is hydraulic conductivity, b is aquifer thickness and i the hydraulic gradient.

The bromate "plume" at this location is approximately 1km wide from the Sandridge dry valley to Fairfolds Farm. To capture the entire width of the plume ($Q/2Q_0$ (Bear, 1972)) an abstraction rate of 26.8Ml/d would be required. To capture the entire plume would therefore require significantly greater abstraction than presently at occurs Hatfield. Since the width of the St Leonard's Court site is approximately 200m, in order to capture this zone an abstraction rate of 5.3Ml/day would be required. These calculation of capture zone width are based upon the assumed applicability of Darcy's law and uniform flow in a homogeneous porous media and this assumption is also inherent in the MODFLOW modelling approach.

Four possible future abstraction scenarios have been defined:

I Continuation of the present state (i.e. a "do nothing") future with Hatfield PWS continuing to operate

II Discontinuation of pumping at Hatfield PWS and operation of a nearer source scavenge pumping borehole

III Continuation of scavenge pumping at Hatfield PWS and the operation of a near source scavenge pumping borehole

IV Hatfield PWS ceases to operate and a near-source scavenge pumping borehole is not constructed

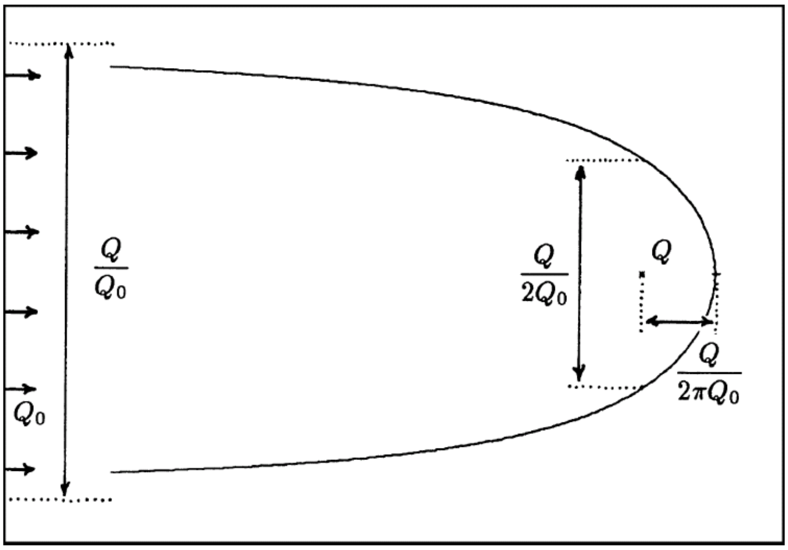
8.1.3 Adopted approach

Four possible source histories and four possible pumping futures have been defined. Additionally, two possible aquifer representations of the karst were defined in Chapter 7; i.e. with and without the karst equivalent porous media extended into the Vale of St Albans. This equates to a total of 32 possible simulations. However, due to the small transport time step required to minimise numerical dispersion in

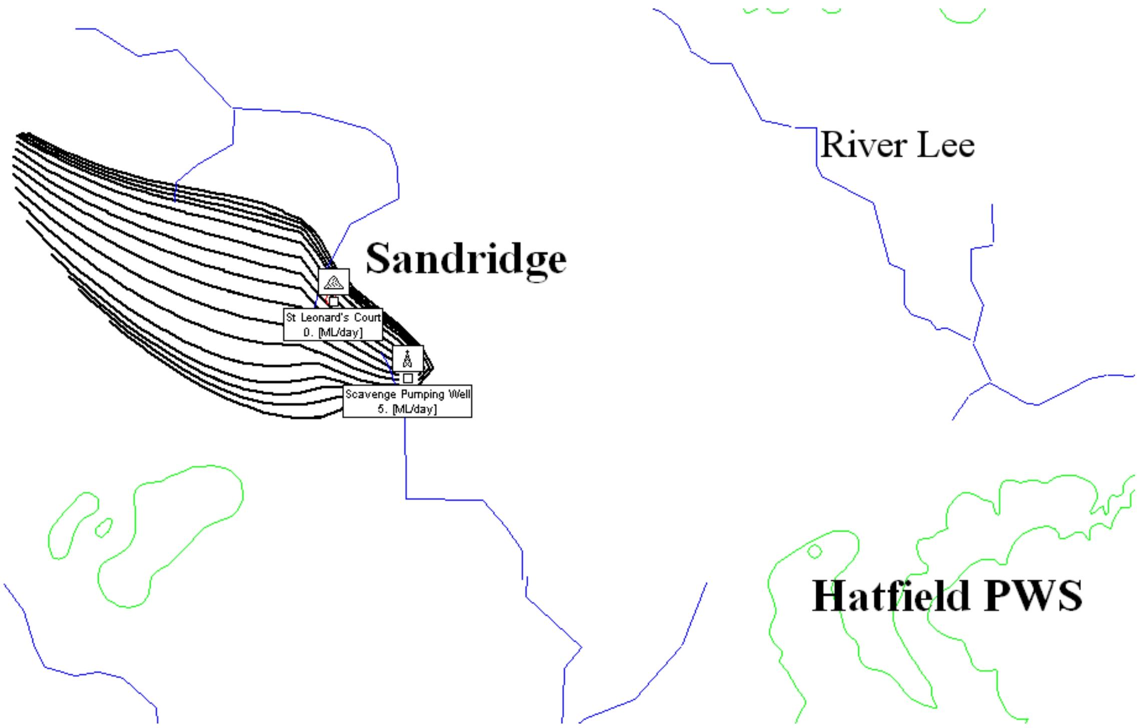
Table 8.1: Summary description of Bromate Solute Transport (BST) simulations conducted in MODFLOW and MT3D-MS

Model Revision	Karst Representation	Source Scenario	Model Stress	Other
BST1	With Vale of St Albans extension	A, C	Converted to multiple steady state stresses and flow model validated against time series data, Future pumping Scenario I (no change) adopted	-
BST2	Effective porosity of karst EPM extension reduced	B	I	
BST3	Karst EPM extension in Vale of St Albans removed	B	I	
BST4	Karst EPM extension in Vale of St Albans removed	B	I	Single domain solute transport
BST5	With Vale of St Albans karst EPM extension	D	I	Also simulated for steady state flow solution
BST6	Karst EPM extension in Vale of St Albans removed	3A, 3B, 3C	I	Increased source terms of Fitzpatrick (2010) by a factor of 3
BST7	Karst EPM extension in Vale of St Albans removed	3B	II	Added hypothetical near source scavenge pumping well

the MT3D-MS solution, model execution times were long ($>$ 10days) and it was not practicable to simulate all possible options. Priority was given to validating the model against observation data through the simulation of possible source histories and aquifer representations. Only the two most likely future pumping scenarios (I and II) were considered for predictive scenarios. In total, ten simulations were conducted, a summary description of which is provided in Table 8.1.



(a) Well Capture Zone



(b) Modelled Capture Zone at Nashes Farm

Figure 8.3: Top - Theoretical dimensions of a capture zone for a well abstraction Q in a uniform flow field Q_0 (Haitjema, 2006). Bottom - Simulated capture zone of a hypothetical scavenge pumping well at 5Ml/day located at Nashes Farm. The modelled capture zone is approximately 1.5km wide at St Leonard's Court. A similar but more efficient scavenge pumping effect could be achieved approximately 400m due north of Nashes Farm using an abstraction rate of 3Ml/day

8.2 Incorporation of Additional Model Stresses

8.2.1 Time Discretisation

In order to be able to incorporate the bromate source histories and future pumping scenarios, the tracer test model which was developed as a steady state simulation based upon long term average aquifer stresses. The model was therefore changed from a steady state single stress period model to a transient multiple stress period model. Although transient flow solution incorporation was developed incorporating aquifer storage, this led to non-convergence of the transport model. As an approximation of transient flow conditions a semi-transient successive steady state simulation was developed, this generates a steady state solution for each stress period based upon the boundary stresses (which can vary with time) for that given period. Although this does not allow for simulation of aquifer storage this appears to be small within the Hertfordshire karst system, since the karst responds quickly to changes to imposed flow stress such as the Hatfield PWS scavenge pumping compared to the monthly variation in model stress. A semi-transient model is therefore considered to be an adequate approximation of the time varying behaviour of the karstic aquifer (Haitjema, 2006) but may be less appropriate for the non-karstic chalk.

8.2.2 Bromate Source

The source history scenarios provided as an annual flux by Fitzpatrick (2010) were converted into daily mass flux rate in μg/day and imported into the model.

8.2.2.1 Recharge

The long term average recharge boundary was converted to a time varying boundary condition using a daily rate of recharge, derived from the 4R model (Entec, 2001) monthly average input between 1965 and 2004. Since 4R recharge simulations were unavailable for the period 2004-2045 an average monthly rate was determined and applied for the stress periods from October 2004, the original end of the validation period for the NNRM). The addition of a variable recharge stress imposes seasonal fluctuation upon the data, which are an essential characteristic of the bromate behaviour and will allow additional validation of the model against observed data.

8.2.2.2 Abstractions and Scavenge Pumping

Abstractions from groundwater wells have also been converted to a time varying stress since this will allow simulation of changes in pumping at Hatfield PWS to simulate the scavenge pumping interim remedial measures. The average monthly abstraction rates for the NNRM (Buckle, 2005) have been adopted and applied as a daily rate from 1965 to September 2004. From 2004-2045 the long term average abstraction rate for the period 1965-2004 was determined and applied for the remainder of the model.

Addition of time varying well stresses also allows representation of the transient changes to pumping, such as the impact of abstraction at Hatfield PWS in reducing down-gradient bromate concentrations. To enable simulation of the changes to abstraction at Hatfield PWS, the time varying stress was altered according to most recent data available for Hatfield PWS for the period July 2005 - May 2008 (prior to July 2005 Hatfield PWS was not in use).

8.3 Validation of the Flow Model

In order to provide confidence in any future predictive modelling scenarios the model must be able to reproduce observed flow and concentration observations.

In Chapter 7, a calibrated flow and transport model was developed based upon steady state simulation of long term average flow conditions and simulation of the 2008 tracer tests. This section describes validation of the time varying model using both an semi-transient and fully transient simulation simulating groundwater storage fluxes. Heads at the same monitoring points as used in Figure 7.8 are presented in Figure 8.4

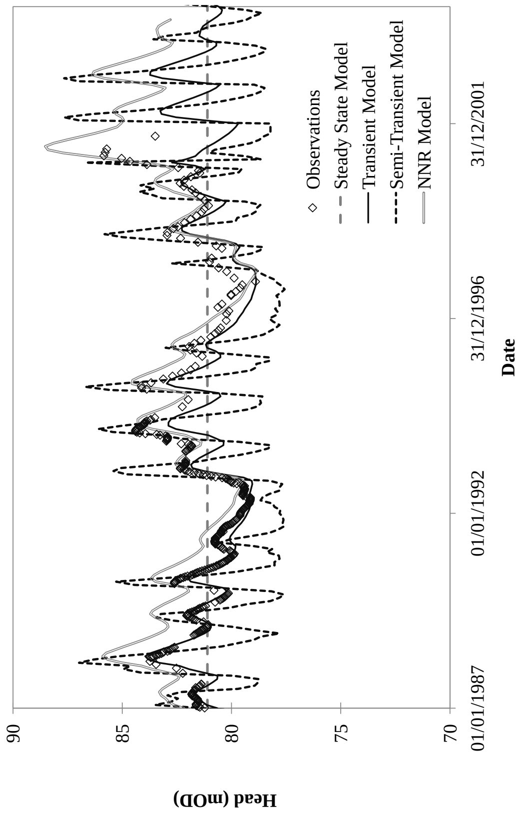
The transient model incorporating groundwater storage and the karst EPM representation replicates the observed seasonal trends relatively well and for the most part also replicates the magnitude of head variations at these locations. Of particular note is lack of seasonality apparent at Robins Nest OBH which is designated as being within the karst zone of the EPM. The high transmissivity of this zone dampens the seasonal variation within and adjacent to it. A similar, but less pronounced effect also occurs at Chelsea cottage which is adjacent to the assigned karst zone within the Lee Valley.

The semi-transient model generally provides a poorer fit than the fully transient model, particularly for locations in the western part of the model where seasonal signal is stronger and the magnitude of seasonal variations is not buffered by groundwater storage in the Vale of St Albans gravels and the errors in the semi-transient model are comparable with the NNRM.

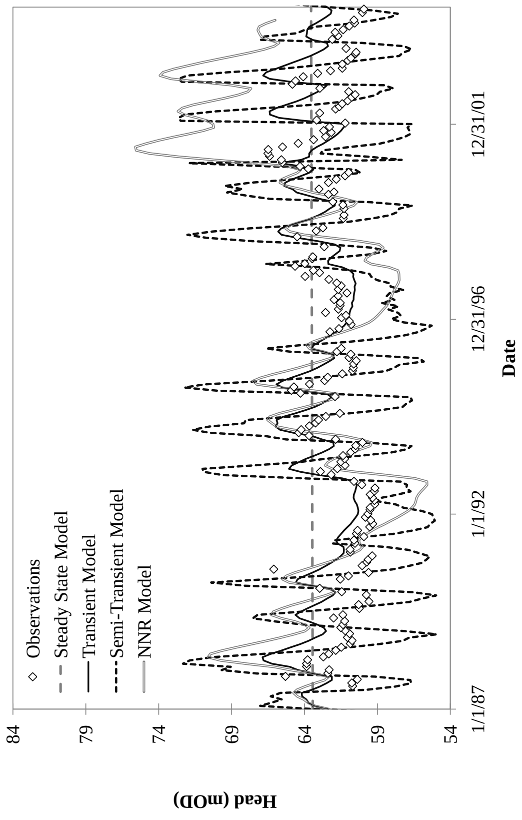
Variations of the modelled river flows are presented in Figure 8.5 for locations on the River Lee.

The seasonal timing of gauged flows are reasonably well captured by the model, however the model does not replicate the variation of observed data, particularly very low or very large flows.

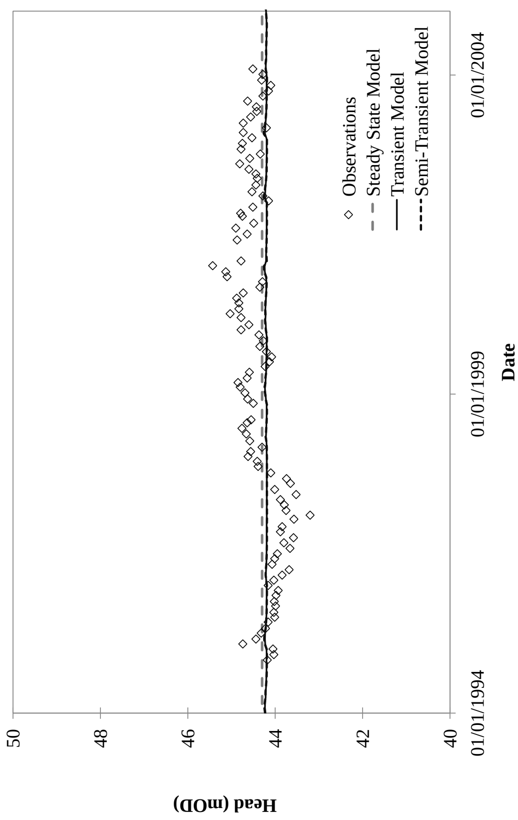
However, since the purpose of the model is to simulate bromate transport and despite these limitations, the general long-term patterns of variation in heads and



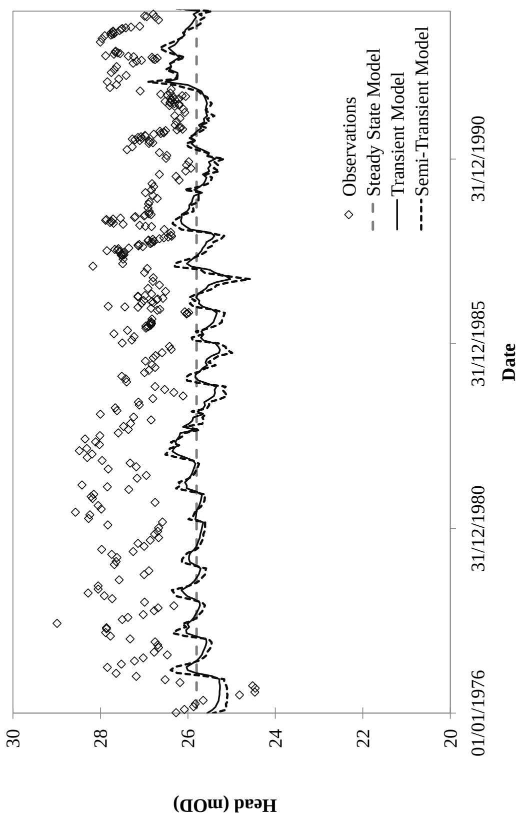
(a) Amwell Corner



(b) North Mymms Park

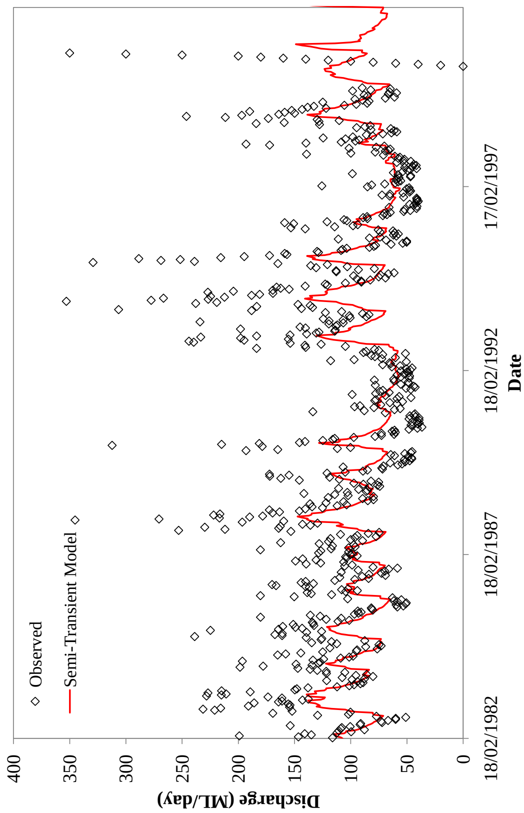


(c) Robins Nest

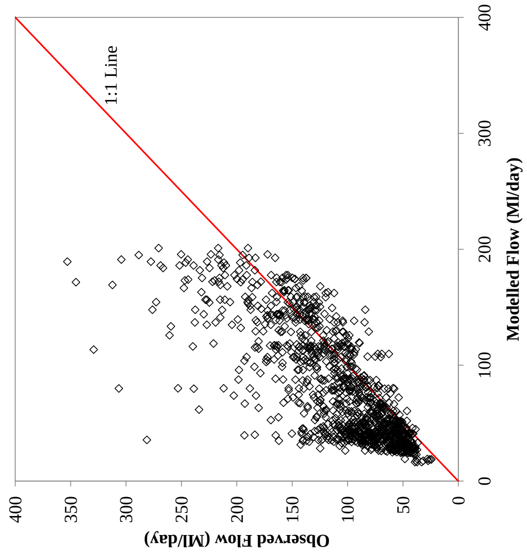


(d) Chelsea Cottage

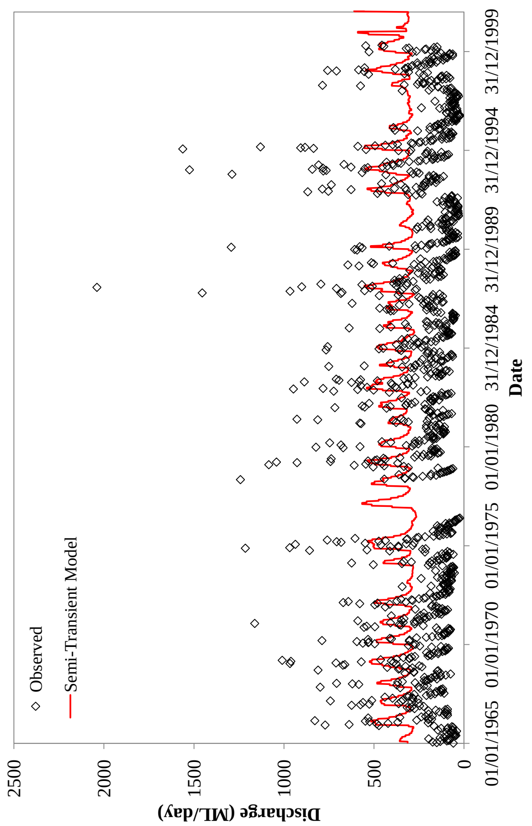
Figure 8.4: Comparison of steady state and transient heads in the calibrated karst model



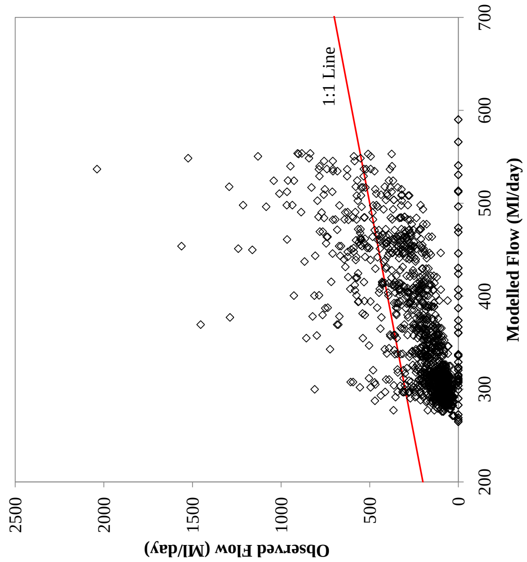
(a) Water Hall Gauge



(b) Water Hall Calibration Plot



(c) Rye Bridge Gauge



(d) Rye Bridge Calibration Plot

Figure 8.5: Comparison of transient modelled and gauged flows in the River Lee

flows is considered sufficiently well replicated; deficiencies in the flow simulation attained are unlikely to lead to a significant error in the transport simulations.

8.4 Transport Model Results

8.4.1 Initial Results (BST1)

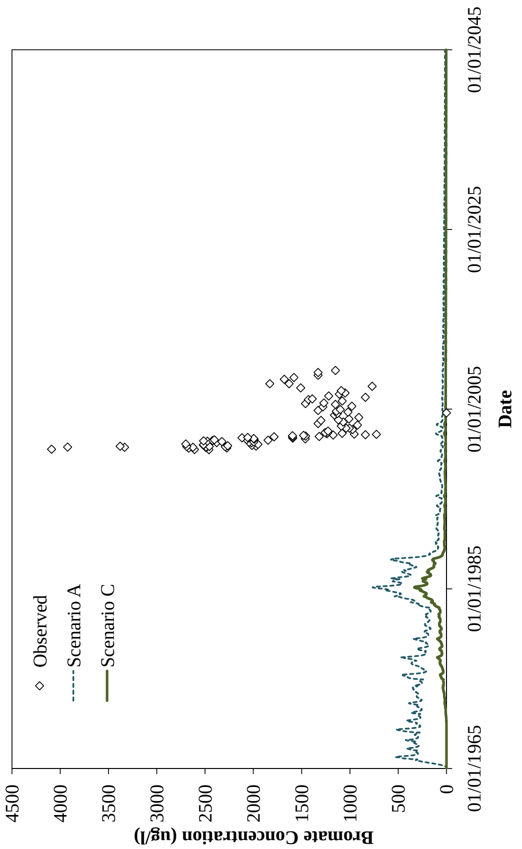
The initial bromate solute transport model (BST1) for the worst and best source scenarios (A and C) used the model aquifer parameterisation determined by the replication of the tracer test modelling, including the westward extension of karst into the Vale of St Albans as described in Section 7.5. Simulated bromate concentrations at the principal sites of interest are presented in Figures 8.6, and 8.7.

The initial model simulation does not capture the observed transient concentration at receptors, in particular the following points are of note:

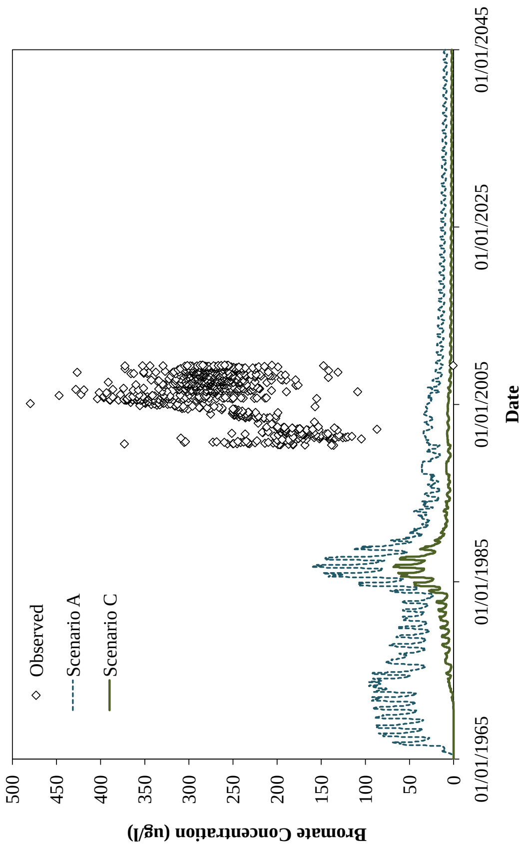
- The peak bromate concentrations are associated with the movement of the 1983-1987 recharge pulse
- The overall magnitude of modelled concentrations is lower than observed bromate at receptors. Source term scenario A provides a closer fit to observed data than scenario C
- Simulation of bromate concentrations at the Northern New River and Lee Valley sites is of low magnitude (typically $\leq 10\mu g/l$). Lynchmill Spring in the central Lee Valley is best replicated, but simulated occurrence of bromate to the north (e.g. Amwell Marsh PWS) and south (e.g. Turnford PWS) is more highly attenuated than observed.
- The trailing edge of the main simulated peak for Scenario B at Nashes Farm is similar to the form of the observed data, showing a sharp drop over a period of less than 1 year which then remains relatively stable for a period of at least 5 years.
- The leading edge of the recharge pulse peak at Hatfield PWS occurs over a period of approximately 5 years, similar to the year on year rise in observation data.

The initial simulations indicate two common trends; modelled concentrations are universally lower than observations, and the timing of peak concentrations precedes that of all apparent observed peaks. However, neither of these limitations alone suggests there are significant deficiencies with the model.

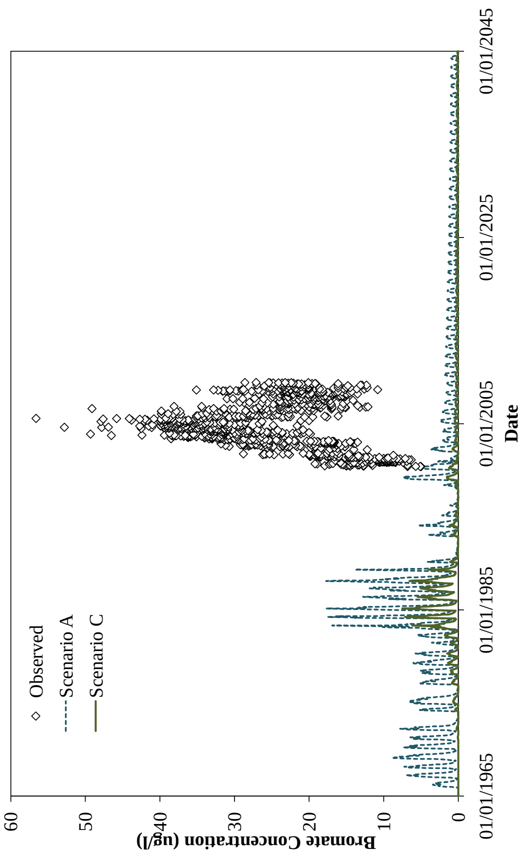
It is important to appreciate that a direct comparison between observed data and model results cannot be made. Simulated concentrations represent a spatially averaged concentration for a porous media grid cell approximately 200m x 200m x



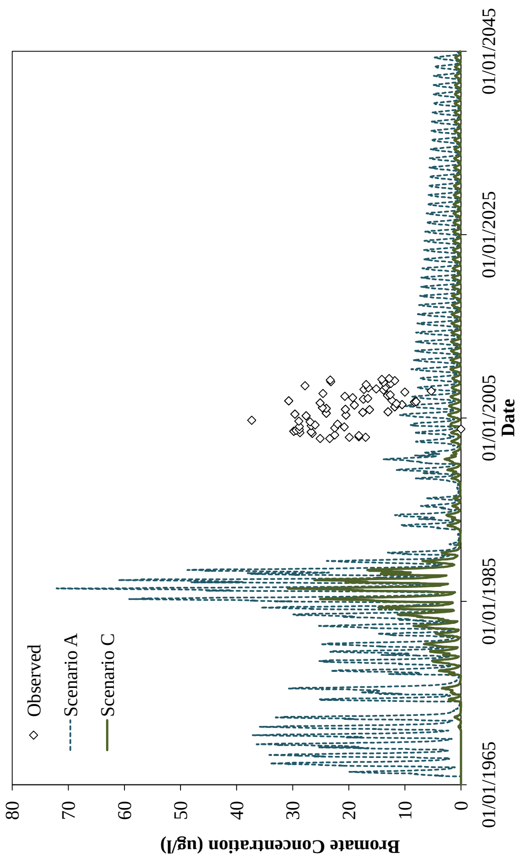
(a) Nashes Farm



(b) Hatfield PWS

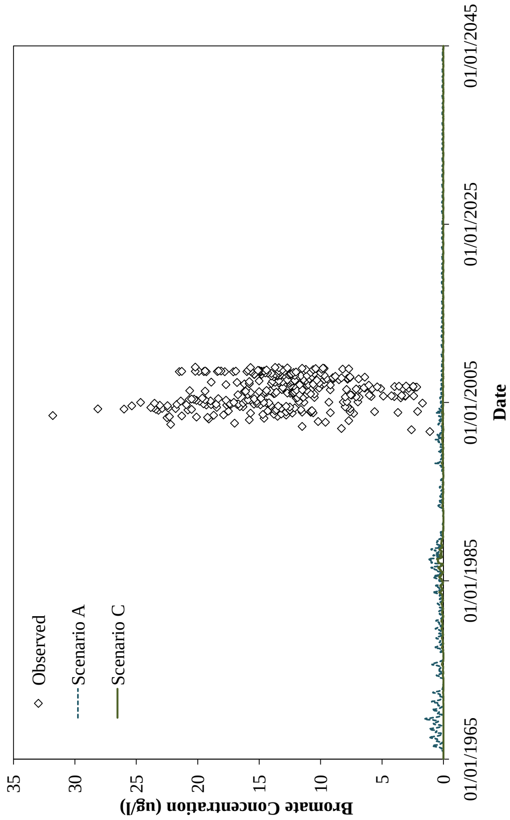


(c) Essendon PWS

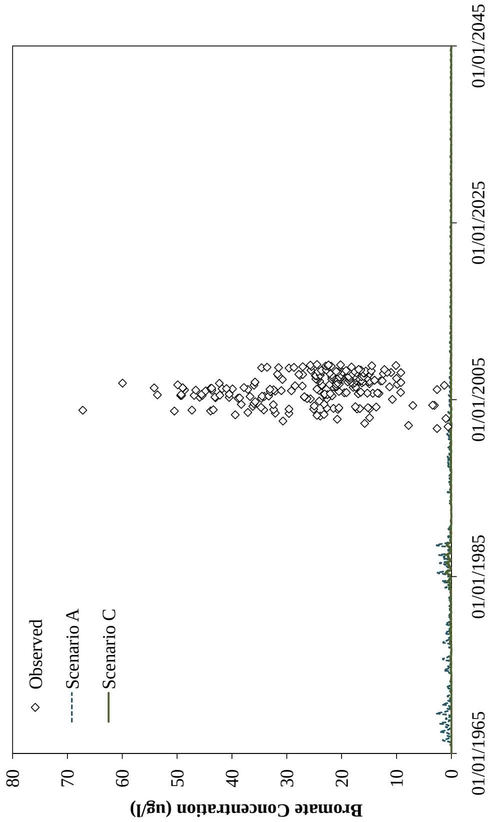


(d) Arkley Hole

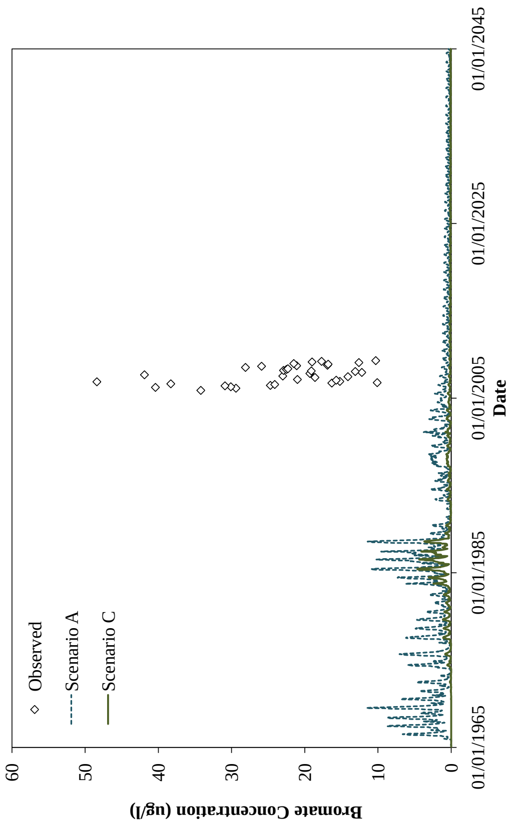
Figure 8.6: Initial simulations of bromate transport (BST1) to target locations between St Albans and Arkley Hole.



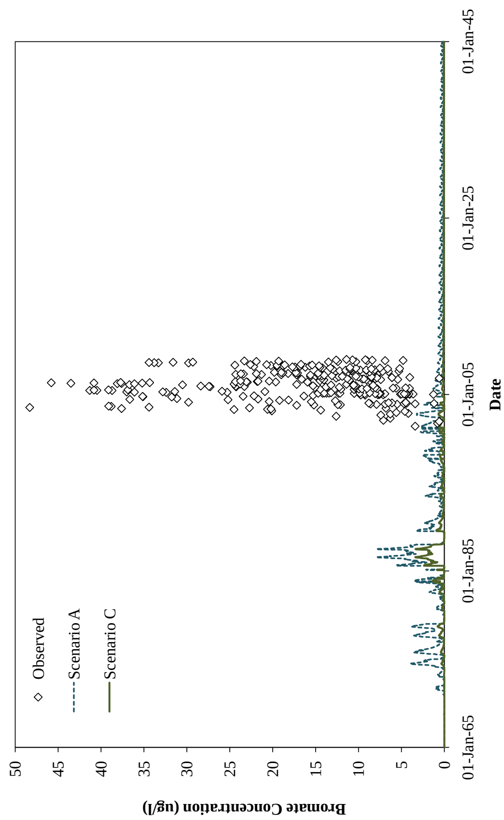
(a) Amwell Marsh PWS



(b) Hoddesdon PWS



(c) Lynchmill Spring



(d) Turnford PWS

Figure 8.7: Initial simulations of bromate transport (BST1) to the Lee Valley

60m. In reality concentrations at observation wells are influenced by the discrete nature of the aquifer and a well may only be supplied by a limited number of bromate-bearing fissures, its water column could be unevenly mixed and it may sample an incomplete portion of the aquifer.

The simulated timing of peak concentrations is due to the progression through the aquifer of the inferred 1983-1987 recharge pulse at the source zone. Available bromate observation data are extremely limited, relating to only to the period 2000-2009 and it is likely that initial breakthrough of bromate at all observation points occurred prior to this date.

Bromate concentrations were generally rising between 2000 and 2005, prior to the operation of the Hatfield PWS scavenge pumping. implying that either a long term increase to a higher concentration is/was occurring, or that that the long term rise represented establishment of new equilibrium following cessation of abstraction from Hatfield PWS, a trend which may now have been reversed by the adoption of long term scavenging.

Tracer tests have provided some constraints on travel times within the Vale of St Albans, which the model has been calibrated to, but bromate may not be being transported along the same flowpaths as the Bacteriophage. By the nature of a non-conservative, potentially sorbing tracer and limited duration of tracer observation, only the fastest low attenuation flow paths would have been indicated by the bacteriophage.

Bromate is likely to be conservative and may have existed in the aquifer for decades, and therefore may be being transported by wider range of both slower and faster, transport routes. Bromate transport is also likely to have be significantly attenuated by dual porosity matrix-fracture exchange which operates on longer timescales.

8.4.2 The Vale of St Albans Karst (Simulations BST2 and BST3)

It is possible that the model may be simulating the form of the bromate transport approximately, i.e. observed concentrations are the result of the 1983-87 site clearance and associated flushing migrating through the aquifer but that the travel time of the pulse is too quick. But, as discussed above such similarities may simply be coincidental since long term (at least on the order of decades) trends in bromate concentrations are unknown.

To investigate if a slower travel time could improve the simulation fit to the data the a case was run for bromate source scenario B which is similar to scenario A, but with an increased mass flux during the recharge pulse.

Initially, the effective porosity of the westward extension of the karst EPM into the Vale of St Albans was reduced to that of the surrounding non-karstic (0.05-

0.03) Chalk (Simulation BST2). Hydraulic conductivity of the extension was left unchanged.

Additionally the model was also run with the entire westward karst EPM removed, with both hydraulic conductivity and effective porosity transport parameters returned to their original values (Simulation BST3). The results from Nashes Farm OBH and Hatfield PWS for both scenarios are presented in Figure 8.8.

The revised simulations show a closer agreement between travel time of the recharge pulse bromate input and observed bromate concentrations at receptors. Conversely, the magnitude of the simulated concentrations is lower. This is due to additional dispersion in the non karstic zone (the original NNR dispersion length of 200m was retained) and increased dual porosity attenuation due to a slower travel time. If present observations and the general rising trend (ignoring the impact of Hatfield PWS scavenge pumping) are due to progressive transport of the inferred 1983-1987 recharge pulse then a non-karstic representation of the Vale of St Albans provides a more appropriate representation of that transport.

Although karstic flow paths, as indicated by the tracer testing, may occur within the Vale of St Albans, the overall contribution to bromate transport may be limited with the long-term transport of bromate occurring principally via non-karstic fracture flow with limited solution enlargement. This is consistent with the 2000-2009 observation data that suggest a relatively stable "plume".

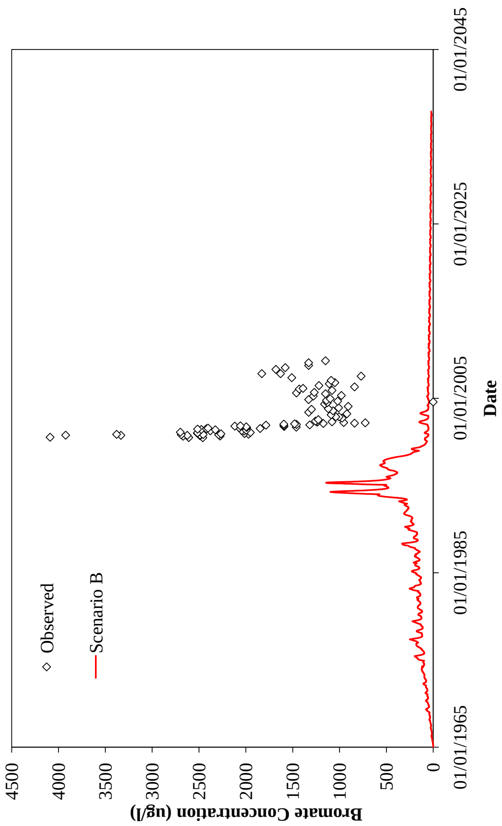
Taking the adjusted travel time resulting from removal of the westward karst extension as approximately correct, the magnitude of simulated breakthroughs remains a problem. Given, that the model simulated transport of both *Serratia Marcescens* and $\Phi X174$ well between Water End, Hatfield and the Lee Valley, and that bromate concentrations are underestimated at Hatfield PWS to the west of the main karst zone implies that either:

- Too much attenuation and dispersion is simulated within the Vale of St Albans area
- Alternatively, the source terms may be incorrect and not enough bromate mass is added to the model, either in total, or in a transient manner through definition of the time varying mass fluxes.

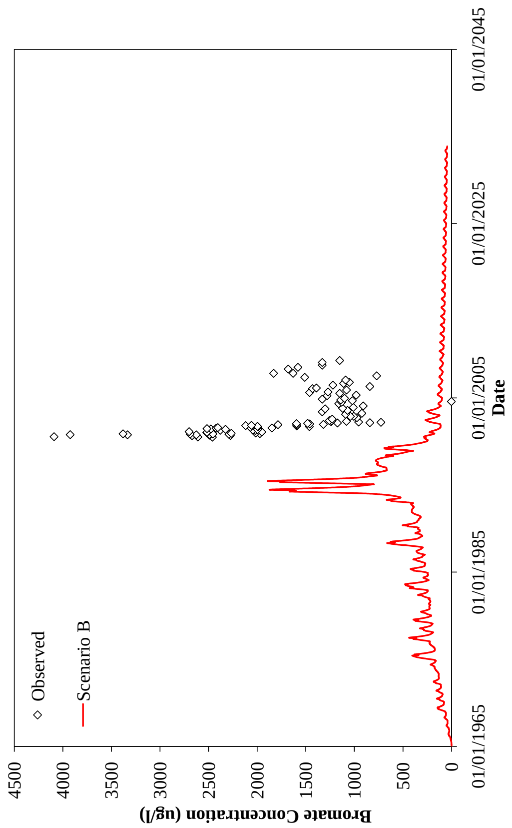
8.4.3 The Effect of Dual Porosity Attenuation

Initial model simulations appear to be affected by too much attenuation and dispersion resulting in underestimation of observed data.

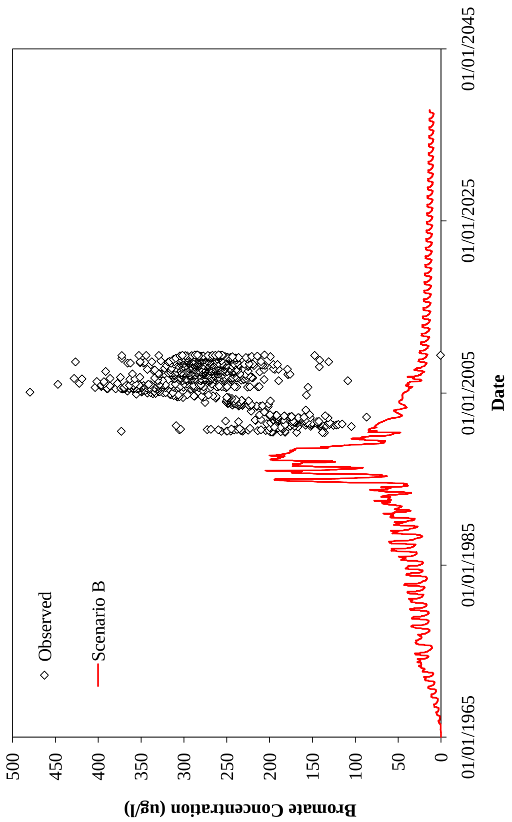
One possibility is that too much dual domain exchange is simulated by the MT3D-MS dual domain first order exchange reaction. The mass transfer coefficient adopted was initially derived from analytical modelling of tracer breakthroughs which suggested a value between 1×10^{-5} and 1×10^{-8}. Calibration of the distributed



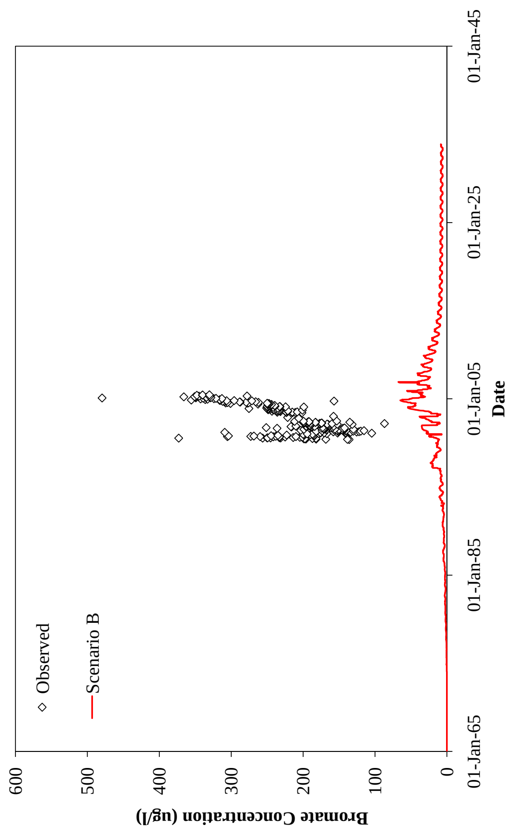
(a) Nashes Farm Simulation BST2



(b) Nashes Farm Simulation BST3



(c) Hatfield PWS Simulation BST2



(d) Hatfield PWS Simulation BST3

Figure 8.8: Simulations for Bromate source scenario B at Nashes Farm and Hatfield PWS removing the Vale of St Albans karst EPM representation

Table 8.2: Equations linking the first order mobile-immobile mass transfer coefficient ω, to physical aquifer properties. Where: θ_{im} is the immobile (matrix) porosity, B is the half block thickness of the matrix slabs, D^*_{im} is the effective diffusion coefficient through the matrix porosity and r_0 is the radius of the matrix spheres.

Parallel Slabs	Matrix Spheres
$\omega = \frac{3\theta_{im}}{D^*_{im}B^2}$	$\omega = \frac{150\theta_{im}}{D^*_{im}r_0^2}$

karst flow and transport model by simulation of tracer transport suggested a value of 1×10^{-6} was appropriate. Mass transfer coefficients can represent a variety of transport processes, not only diffusive transfer but temporary entrapment in immobile zones, and temporary sorption. However, the parameter only has a limited physical basis (Neville, 2006) and effectively is a fitting parameter.

These mass transfer coefficients were based on a relatively short duration tracer test, whereas the bromate contamination represents longer term processes of solute transport. The matrix volume and fracture porosity available to the phage and the bromate are likely to be significantly different and it follows that the degree of dual porosity exchange will also differ.

In calibrating the tracer test model, the bacteriophage tracers were considered to be non sorbing based upon the literature data presented in Section 5.2.1.1. Sorption is likely to be limited within karst conduits where the contact time and opportunity to interact with the surrounding rock is limited (Field and Pinsky, 2000) but if a limited degree of sorption did occur it might have been masked as a process by the mass transfer or inactivation. When applied to the conservative bromate solute, the simulation might be more attenuated by the above processes than occurs in reality.

The magnitude of diffusive exchange is also likely to differ between the karstic flow paths, where an effective mobile-immobile first order exchange might be a more appropriate model, and the matrix-fracture system where diffusive flux is likely to be more significant. Given that the modelled karst representation within the Vale of St Albans has proven inaccurate, there may be a case to adopting spatially varying mass transfer coefficients, to represent these differences.

There is also uncertainty as to whether bacteriophage can actually participate in true diffusive exchange with the chalk matrix. Although there is no physical basis with respect to the relative size of the viruses and the chalk matrix pore throats on which such exchange can be ruled out, there is currently no available experimental data to suggest that such diffusion occurs. If phage are susceptible to diffusive exchange, they are likely to have different effective diffusion coefficients to bromate, which will cause their diffusive flux and therefore the form of the progression through the aquifer to differ.

Van Genuchten and Dalton (1986) has provided two physical definitions for the mass transfer coefficient ω in an idealised fractured media, which can be represented as a either a series of parallel matrix slabs separated by fractures or by matrix spheres surrounded by fracture porosity.

Immobile porosity in the model has been taken to be 38% based upon site investigation at St Leonard's Court, Sandridge (Buckle, 2002) and is consistent with that for the Lewes Nodular and Seaford Chalk Formations (see Section 3). An effective diffusion coefficient for bromate of 1.57×10^{-4} was adopted based upon Buckle (2005).

The mass transfer coefficient in the original NNRM was 5×10^{-6} for which sensitivity was assessed by varying by two orders of magnitude either direction (Buckle, 2005). Watson (2004) used values between 1.65×10^{-4} and 5.28×10^{-7} for the transport of chloride in the Kent Chalk aquifer assuming a slab geometry with fracture spacing between 0.36 and 5.83m.

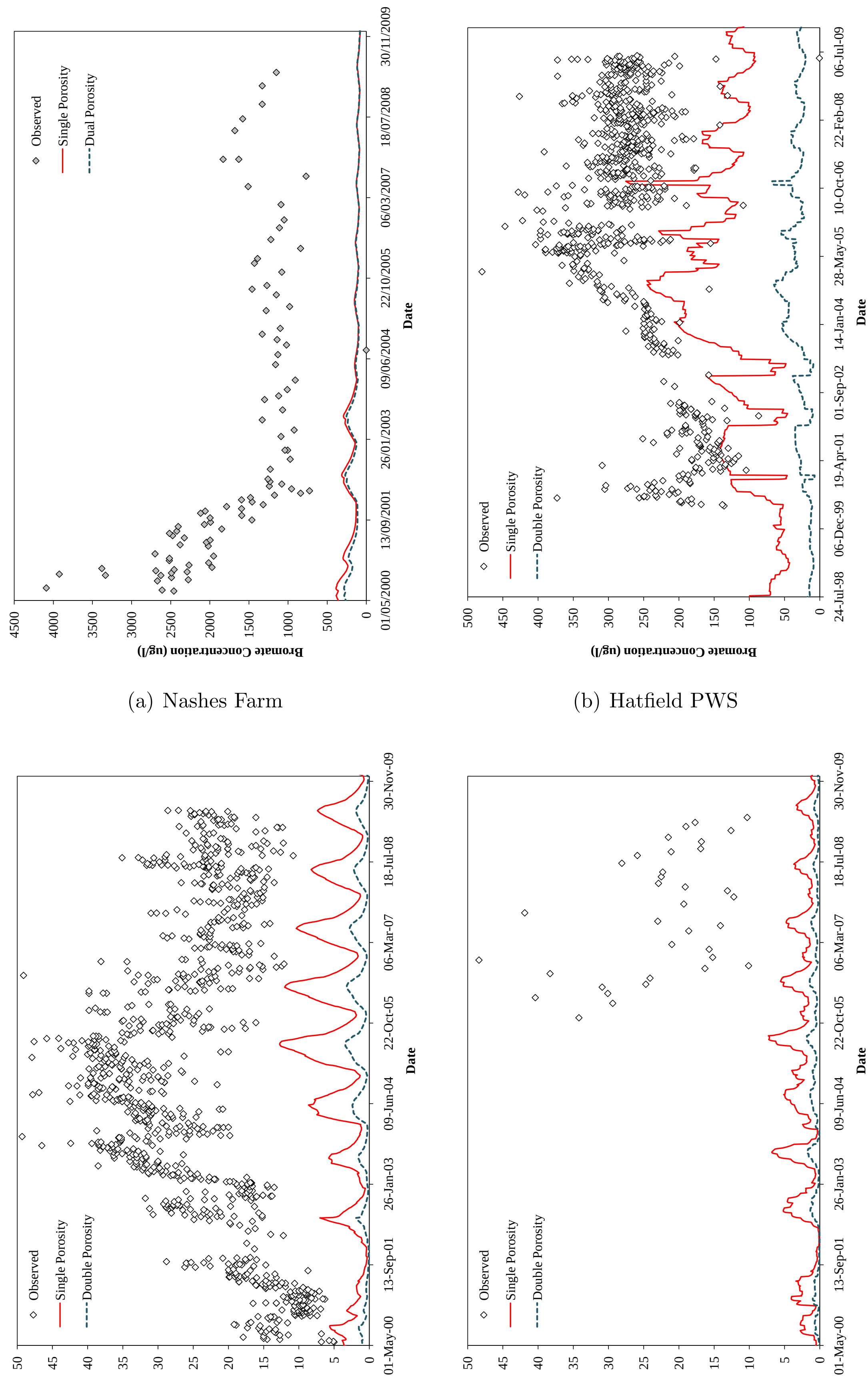
Despite the possible differences in the transport behaviour of bacteriophage and the bromate solute, mass transfer coefficients derived from the analytical modelling of tracer breakthrough are not significantly different from other estimates for the solute transport in chalk.

The tracer derived mass transfer coefficient is lower than that adopted in the NNR bromate model and result in less attenuation, therefore differences in representation of dual porosity attenuation are unlikely to be the cause of the apparently underestimate bromate concentrations at receptors in model simulations BST1, BST2 and BST3.

To investigate the significance of the first order mass transfer, a model simulation was developed for source Scenario B with the dual domain process switched off (Simulation BST4). This is a conservative single (effective) porosity model with advection and dispersion as the only transport processes. Results for Nashes Farm, Hatfield, Essendon PWS and Lynchmill Spring are presented in Figure 8.9.

The single domain results provide a closer fit to observed concentrations indicating the dual domain process accounts for a reduction in simulated concentrations. The effect becomes more significant downgradient and is least significant at Nashes Farm where travel times are shortest. However, since the mass transfer coefficient adopted is lower than previous models, on the basis of these comparisons dual porosity attenuation is not considered to be a significant factor in causing the low simulated concentrations relative to other models.

The first order mass transfer process in MT3D-MS is only an approximation of true diffusive exchange and particularly when travel times are fast in relation to the diffusion time. In addition, first order mass transfer is capable of approximating many other transport processes including karst immobile-mobile partitioning. The estimates of an appropriate mass transfer coefficient cannot be easily improved beyond the range suggested by the tracer testing and empirical estimates, particularly for regions of the aquifer where diffusive exchange is significant. A much longer duration tracer test is required in order to improve confidence in the estimate for the fracture-matrix system



(a) Nashes Farm

(b) Hatfield PWS

(c) Essendon PWS

(d) Lynchmill Spring

Figure 8.9: Comparison of of bromate transport using source scenario B and a single (Simulation BST4) and dual domain (Simulation BST3)

A possible alternative explanation for low simulated concentrations in models BST1-4 could be the scale of mechanical dispersion. The dispersion length 200m from the original NNRM (Buckle, 2005) has been retained in these models except in the zone designated as the karstic, where a value of 25m was applied using the tracer test observations. This lower value should result in less dispersion, particularly where karstic effects dominate between Hatfield and the Lee Valley.

Since simulated bromate concentrations at Nashes Farm and Hatfield PWS are underestimated by initial models, so are concentrations downgradient. This implies that a process upgradient of both locations is incorrectly represented. Since, in the absence of any new data, the parameters governing flow and transport within the Vale of St Albans have been largely unchanged from the original NNRM and that transport parameters within the karst zone have been adjusted to provide less dispersion and attenuation than previous models, this implies the scale of bromate release may be under-represented by the source scenarios.

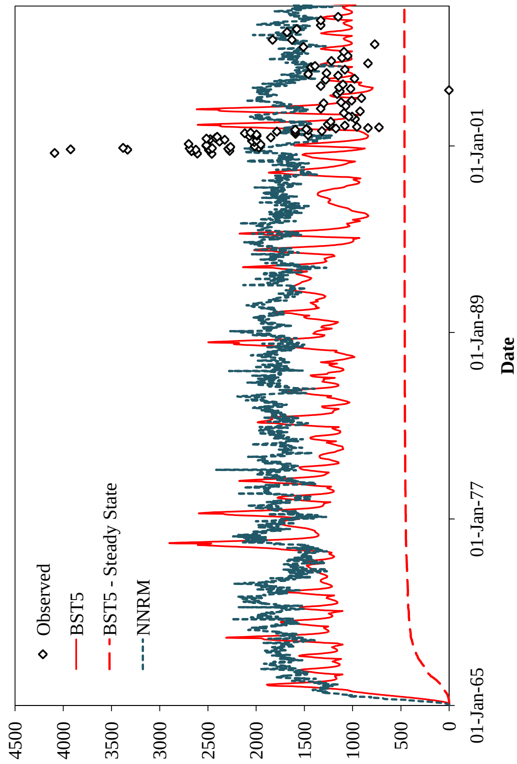
8.4.4 The Effect of the Bromate Source term

Simulations BST1-BST4 suggest that the bromate source terms may themselves be underestimated and that this impacts upon simulated concentrations at receptors throughout the model. The source terms are based upon a analysis of likely release scenarios derived from extremely limited data which can be interpreted in a number of possible ways (Fitzpatrick, 2010).

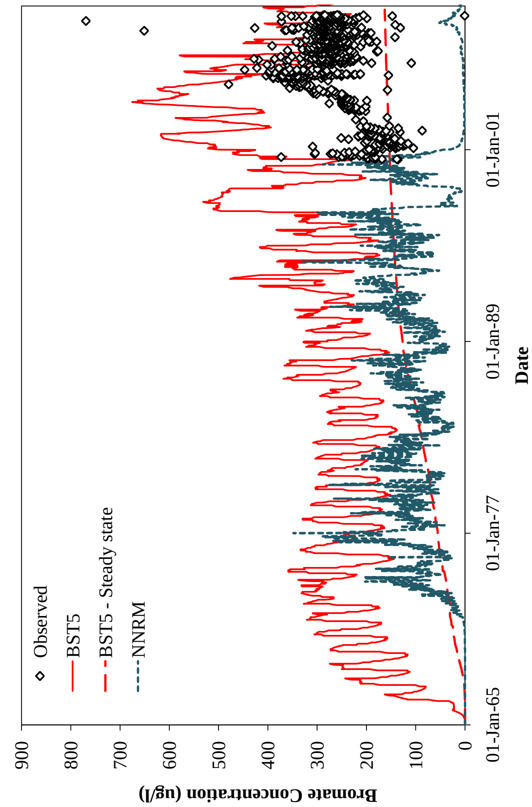
The original NNRM and source term provided a reasonable of the spatial distribution and magnitude of the bromate "plume" between Sandridge and Hatfield (Buckle, 2005), which is the area that appears to be deficient in the new karst model. To check the consistency of the new karst EPM model, the simulation was re-run using the NNR source term (Simulation BST5), a constant concentration of $5000\mu g/l$. All other parameters were kept consistent with the initial calibrated karst model, i.e. including dual porosity mass transfer and the westward karst extension in the Vale of St Albans. The original NNR source is an extreme simplification of reality since it does not provide a realistic mass balance nor allow temporal variations of flux.

It does allow direct comparison of the NNR and new karst EPM representation and provides a significantly larger bromate source term that allows the aquifer to achieve a pseudo equilibrium allowing comparison with the time-varying mass fluxes of Fitzpatrick (2010). The results of the model simulation BST5 along with those of the Original NNRM are presented in Figures 8.10 and 8.11.

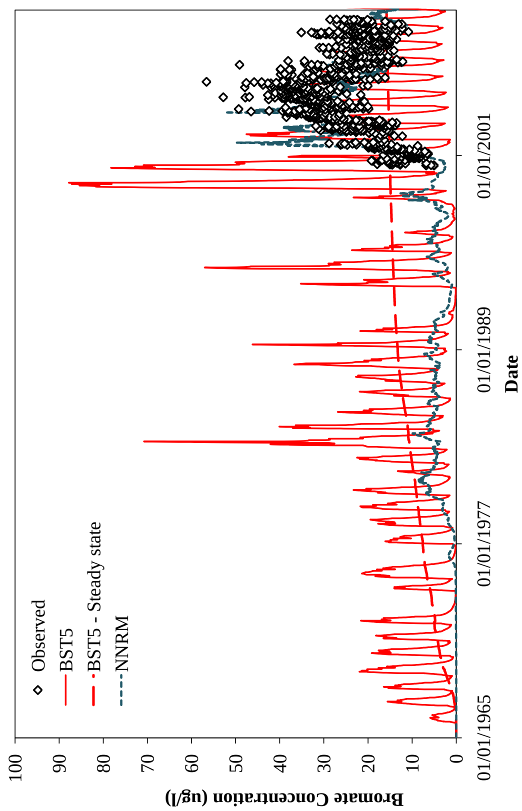
In comparison to the NNRM, the karst EPM predicts much earlier breakthrough at receptors due to the faster advective velocities in the karst system and the westward extension of the karst across the Vale of St Albans. Simulated concentrations are also significantly higher in this representation than for other source scenarios



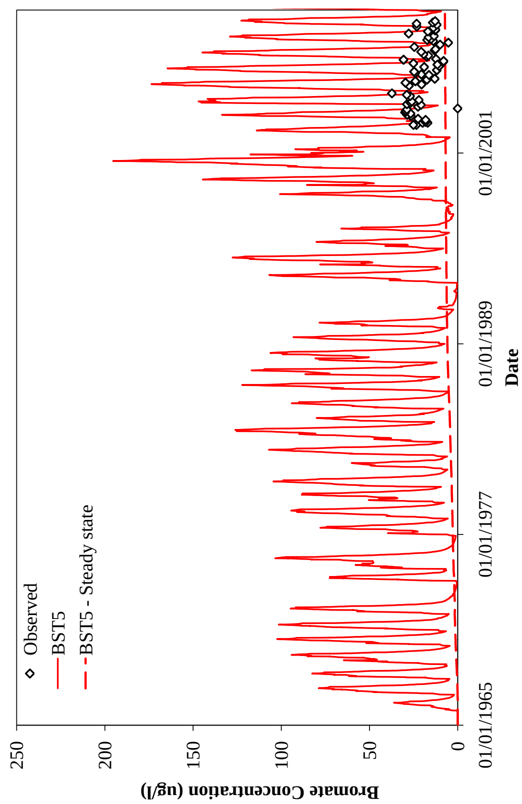
(a) Nashes Farm



(b) Hatfield PWS

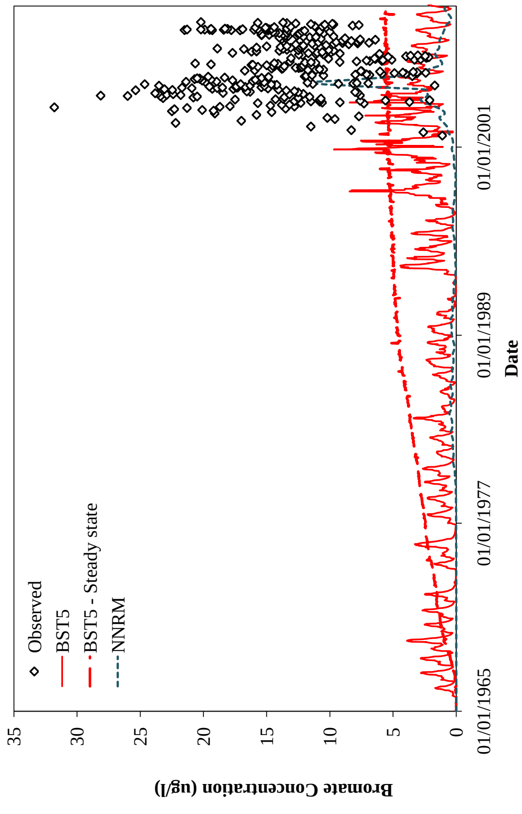


(c) Essendon PWS

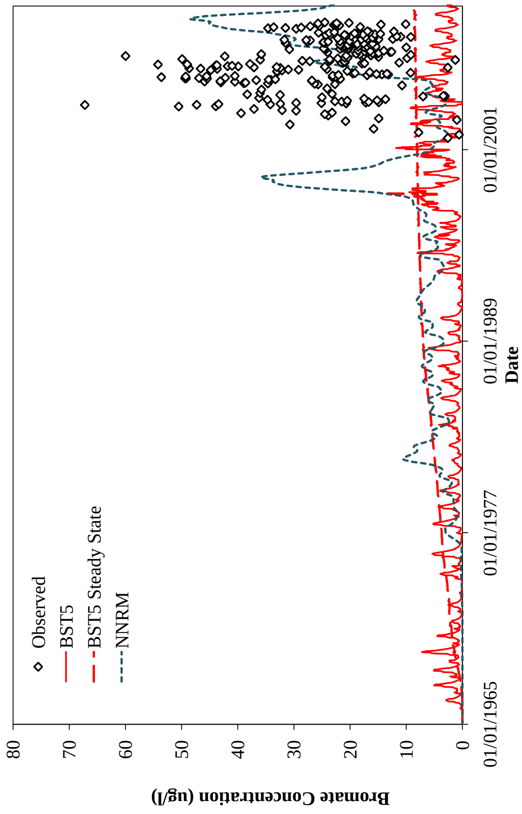


(d) Arkley Hole Spring

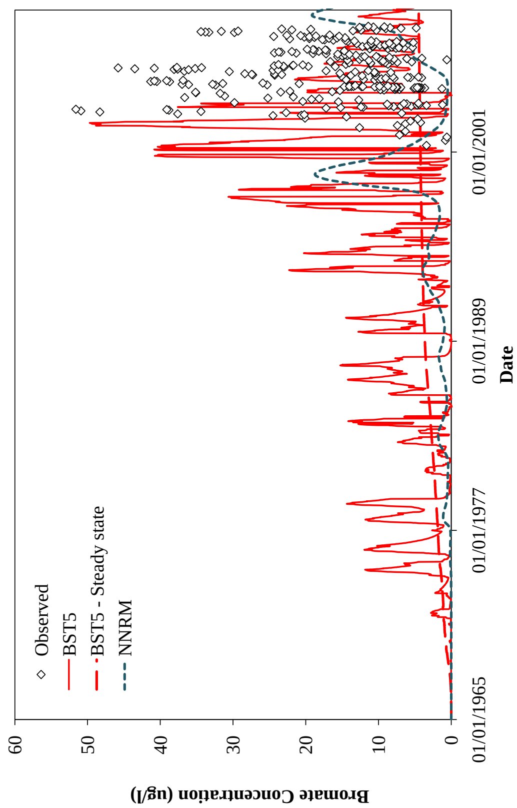
Figure 8.10: Simulations of bromate transport using the karst EPM (Simulation BST5) and a constant concentration source of $5000\mu g/l$. The results of the NNRM and for a steady state representation of the karst model are shown for comparison



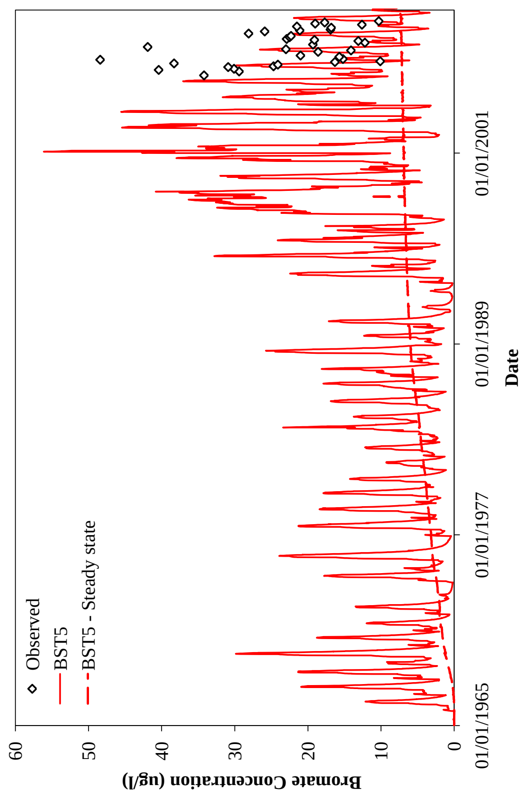
(a) Amwell Marsh PWS



(b) Hoddesdon PWS



(c) Turnford PWS



(d) Lynchmill Spring

Figure 8.11: Simulations of bromate transport using the karst EPM (Simulation BST5) and a constant concentration source of $5000\mu g/l$. The results of the NNRM and for a steady state representation of the karst model are shown for comparison

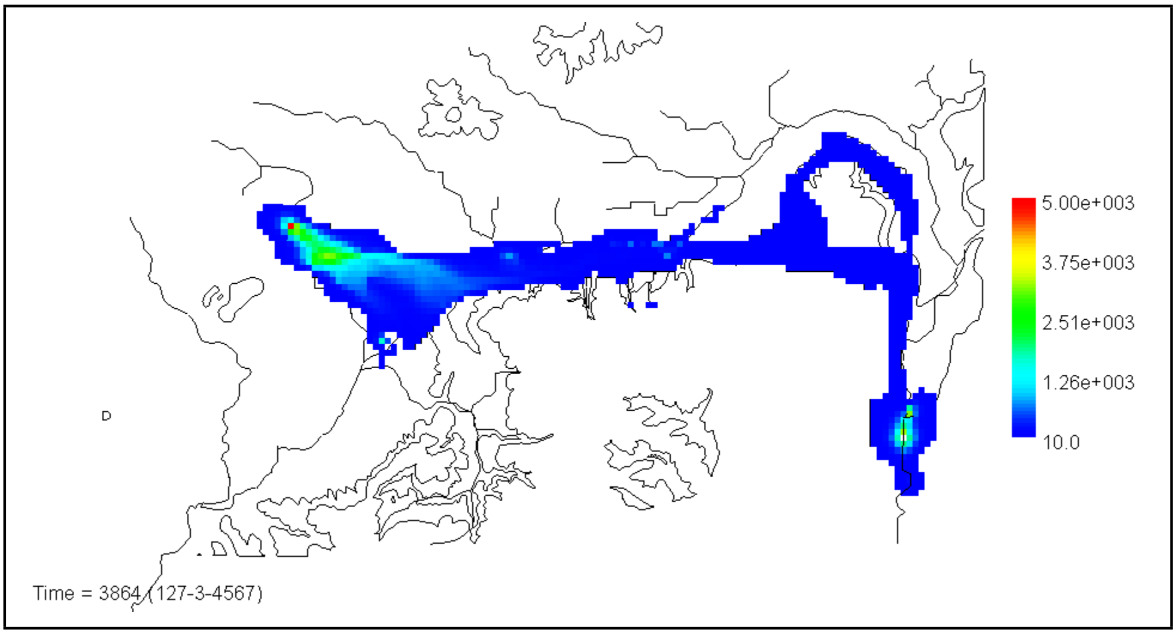


Figure 8.12: Spatial distribution of bromate after approximately 10 years in simulation BST5 utilizing a constant concentration source of $5000\mu g/l$. The plume contour is at $10\mu g/l$. A stable plume is achieved after approximately 1 year of travel time across the Vale of Albans and reaches the Lee Valley after 2 years. Thereafter a pseudo-equilibrium is achieved with transport to the Lee Valley being strongly influenced by seasonal variations and dilution during the winter months. Note the high concentration stagnant zone south east of Turnford PWS, This is modelling artifact due to low hydraulic conductivity and piezometery but does not appear to affect concentrations at observation locations

reflecting the greater mass input (between 9-11kg/day) required to maintain source concentrations at $5000\mu g/l$ in the source cell. Simulated concentrations are also more consistent with observations, at both Vale of St Albans Locations and the Lee Valley. The spatial variation, presented in Figure 8.12 apparent in the Lee Valley bromate concentrations is also reproduced with higher concentrations in the Southern Wells of the Lee Valley (Hoddesdon-Turnford) than in the northern wells (e.g. Amwell Marsh PWS, Rye Common PWS).

Since the karst EPM model works well with the constant concentration source, and as described in section 8.4.3, attenuation from dual porosity mass transfer and/or dispersion is not considered to be causing the model to underestimate concentrations relative to the previous parameterisations, it is likely that a larger mass input of bromate should be represented.

Whilst the constant concentration source is unrealistic in terms of the total mass input and of its temporal variation, that realistic concentrations can be achieved at receptors suggests that for at least some of the source history the mass flux could have been of similar magnitude to that of the constant source, i.e. a mass flux $9-12$kg/day is required for at least 5 years. The scenarios A, B and C of Fitzpatrick (2010) represent total bromate mass injections of 24.8, 22.8 and 5.4tonnes between 1955 and 2100. This is equivalent to a daily input of ≤ 0.1 to 6.2kg/day with the highest values occurring for all source terms in the period 1983-1987 when the site

Table 8.3: Calculation of the possible volumetric flux of a saturated aqueous solution required in order to provide the mass input of bromate to create the source terms of (Fitzpatrick, 2010). * Solubilities taken from (IPCS, 2006) ** 1 Mole of Bromate (BrO_3) is equal to 127.886g. *** Assumes discharge occurs at a single daily rate for the 25 year (9125 day) period of factory operations from 1955-1980.

Ion	$NaBrO_3$	$KBrO_3$
Solubility in water (g/100ml at 20^o C)*	36.4	7.5
1 Mole of Saturated Solution (ml)	414.5	2226.45
Number of Bromate Moles**		
Scenario A (24.8 tonnes)	193905.5	148533.2
Scenario B (22.8 tonnes)	177927.2	136554.7
Scenario C (5.4 tonnes)	42400.3	32341.9
Volume of Solution Required (l)		
Scenario A	80373.8	431720.9
Scenario B	73750.8	396146
Scenario C	17574.9	94402.15
Daily Input Rate (l/day)***		
Scenario A	8.8	47.3
Scenario B	8.1	43.4
Scenario C	1.9	10.3

was free of hardstanding.

If, as suggested by the initial modelling, it is assumed that the 2000-2009 rising concentration trends at observations points represents the transport of the 1983-1987 recharge pulse at St Leonard's Court through the aquifer, i.e. the transient description of source flux is correct but the magnitude is incorrect, adjustment of the mass input of the pulse to rates similar to those of the constant source is required. However, it is important to consider if there is any additional justification in doing so.

One consideration is the chemistry of compounds likely to have been in use at the factory and therefore the potential mass flux to the ground that might have occurred. It is known that part of the St Leonard's Court site was used for the storage of solid bromine. The most common industrial products containing bromate are Sodium and Potassium Bromate, these are available commercially from chemical suppliers in a solid form at over 99% purity (e.g. Synatech, 2009). The highest bromate concentrations on the St Leonard's Court site are focused around a former sump, impling that the majority entered the aquifer in a liquid state. Table 8.3 presents possible discharge volumes of $NaBrO_3$, and $KBrO_3$ that would be required to provide enough mass for each source term during the lifetime operation of the factory (1955-1980) assuming discharge is of a saturated aqueous solution.

Although these calculations represent an extremely simplified case they demonstrate that a catastrophic discharge of bromate bearing solution need not be required in order to generate realistic source terms. A 12 kg of Bromate per day mass flux as inferred from the constant concentration source term simulation would require a volumetric discharge direct to groundwater of only 38.9l of a saturated solution of $NaBrO_3$ per day.

A volumetric discharge on the order of 10's of litres per day could easily represent discharge of just a few typical 10l volume buckets and conceivably could arise from the flushing or washing down of equipment. More highly concentrated non-aqueous liquors could contribute a much higher mass input at a lower volume. A catastrophic high volume release may also have contributed significant additional mass to the aquifer.

Whilst not intended to be a robust evaluation of a likely source term, these calculations do demonstrate that there is potential scope to increase the mass flux source terms of (Fitzpatrick, 2010) and retain a physically plausible mass input in order to reconcile the implications of the catchment scale transport modelling. Comparing the initial simulated concentrations for the migration of the 1983-1987 recharge pulse with observations at Nashes Farm and Hatfield PWS suggests that increase in the mass input by a factor of 3 or more should give concentrations at the correct order of magnitude. This would supply a peak mass flux input for the 1983-1987 recharge pulse of between 15.7 kg/day, 18.8 kg/day and 6.6kg/day for scenarios A, B and C respectively.

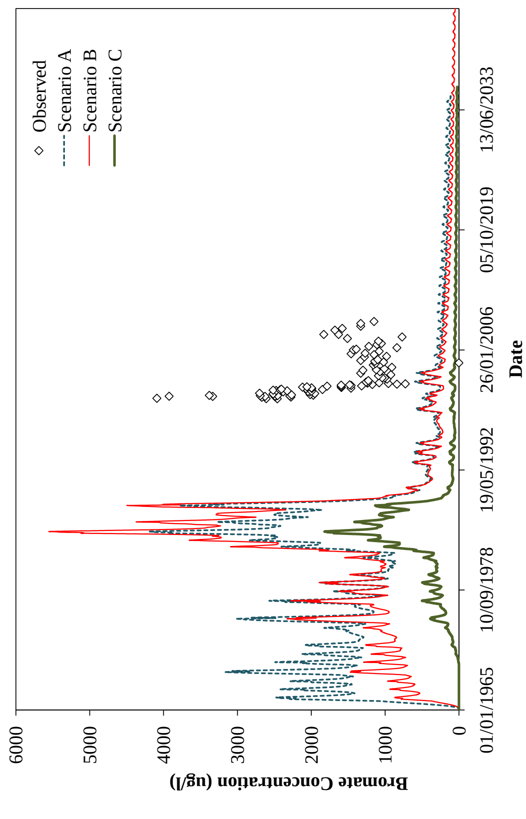
8.4.5 Increased Source Terms (Simulation BST6)

The model simulation was run again using these increased source terms (Simulation BST6). To achieve correct travel times the westward karst extension into the Vale of St Albans was removed (see Section 8.4.2) but the dispersivity of the karst system was retained in the Vale of St Albans. The results are presented in Figures 8.13, 8.14 and 8.15.

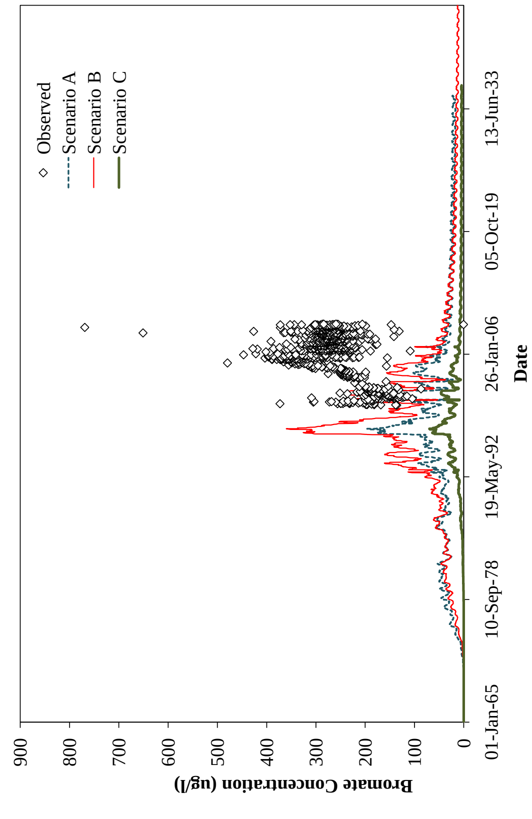
The spatial distributions indicate that the general shape of the plume within the Vale of St Albans is reasonably well replicated forming the elongate teardrop shaped "plume" that is widely inferred to exist in the area. The size and shape of the Vale of St Albans plume varies little with the transient stresses of the model, which is also in accord with the observed stability of the plume. The width of the plume is slightly larger than is observed when compared with Figure 2.1 extending to the headwaters of the Colne (but note that occasional groundwater observations do occur in area).

East of Hatfield, the modelled geometry of the karst EPM is well replicated by the distribution of bromate extending sub-parallel to the River Lee and cutting across the Lee loop to the Lynchmill Spring and Hoddesdon area. Some occurrence of bromate north of the River Lee and northeast of Arkley hole in a zone sub-parallel to the Lee is suggested to occur.

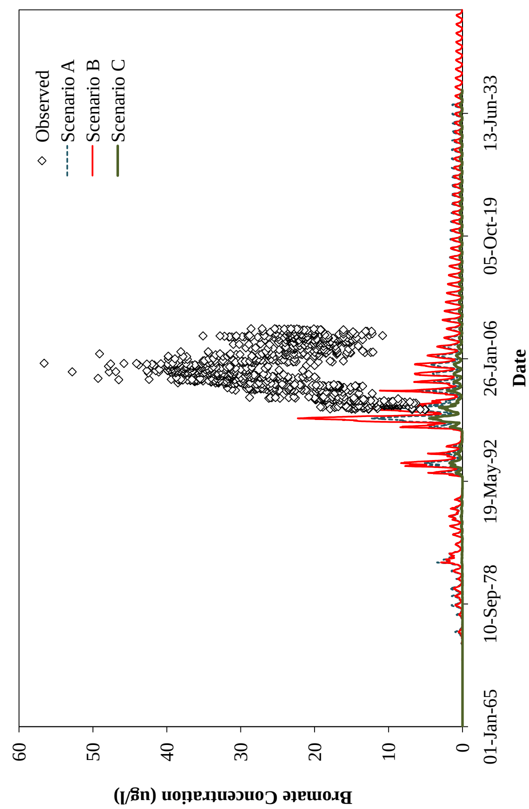
When increased by a factor of 3, bromate source scenarios 3A and 3B show a similar shape and magnitude of plume reflecting relatively little difference in bromate mass flux, particularly from the 1980's onward. The much lower mass flux Scenario 3C generally cannot achieve a sustained breakthrough (at measurable concentrations $\geq 1\mu g/l$) to Lee Valley locations.



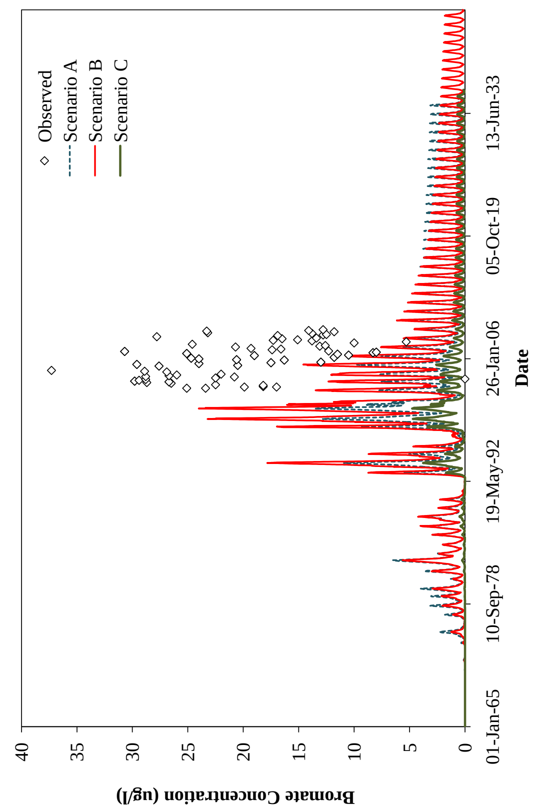
(a) Nashes Farm



(b) Hatfield PWS

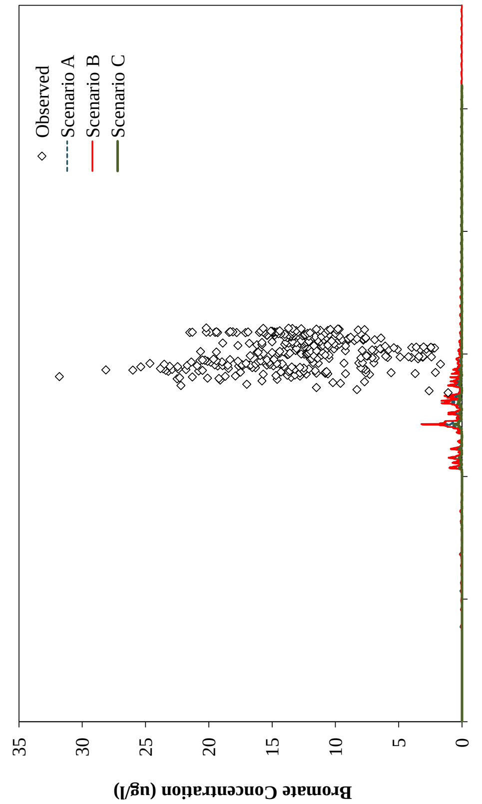


(c) Essendon PWS

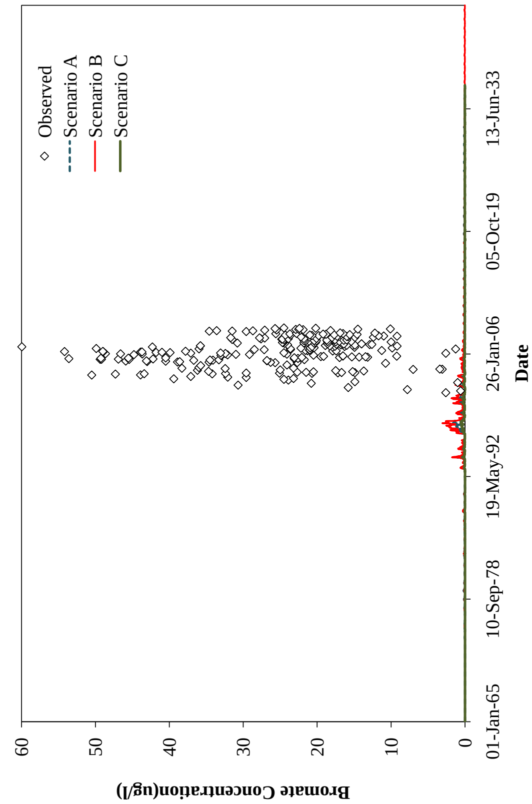


(d) Arkley Hole Spring

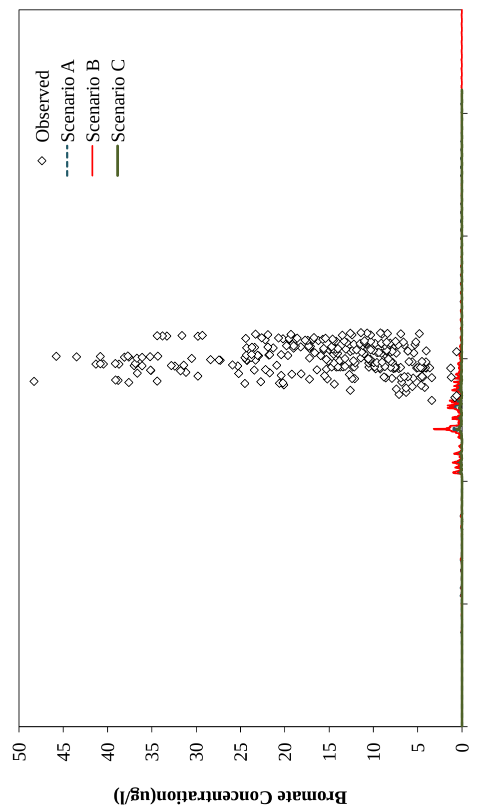
Figure 8.13: Simulations of bromate transport (BST6) using the modified source terms of (Fitzpatrick, 2010) at locations between Sandridge and Arkley Hole Spring



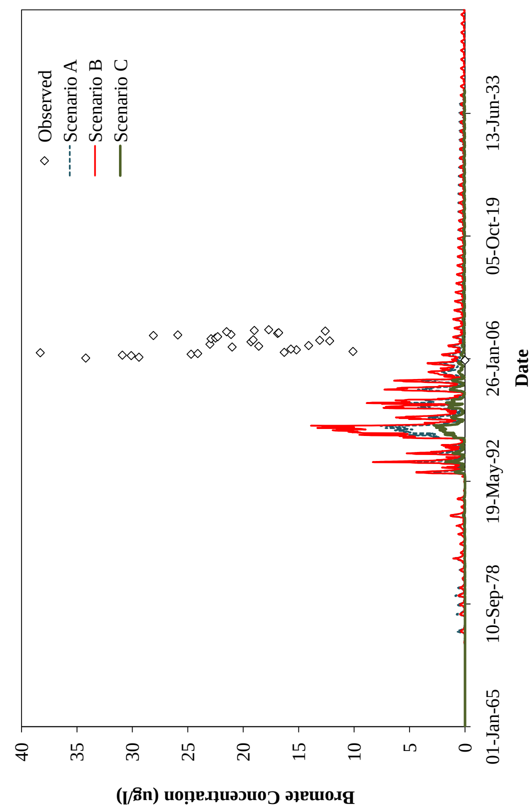
(a) Amwell Marsh PWS



(b) Hoddesdon PWS

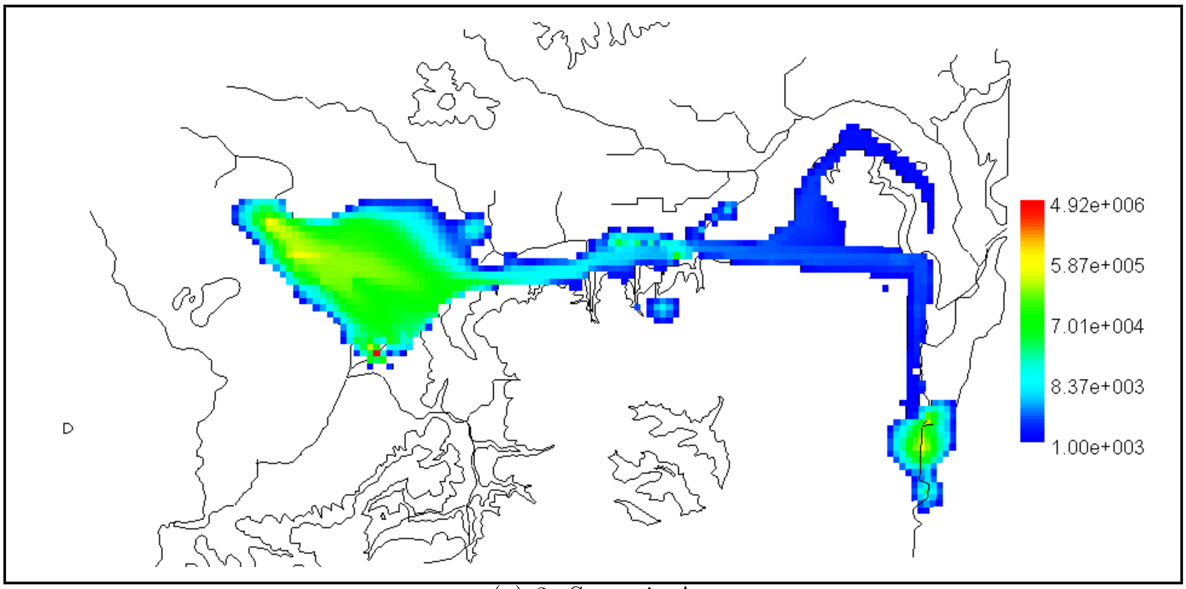


(c) Turnford PWS

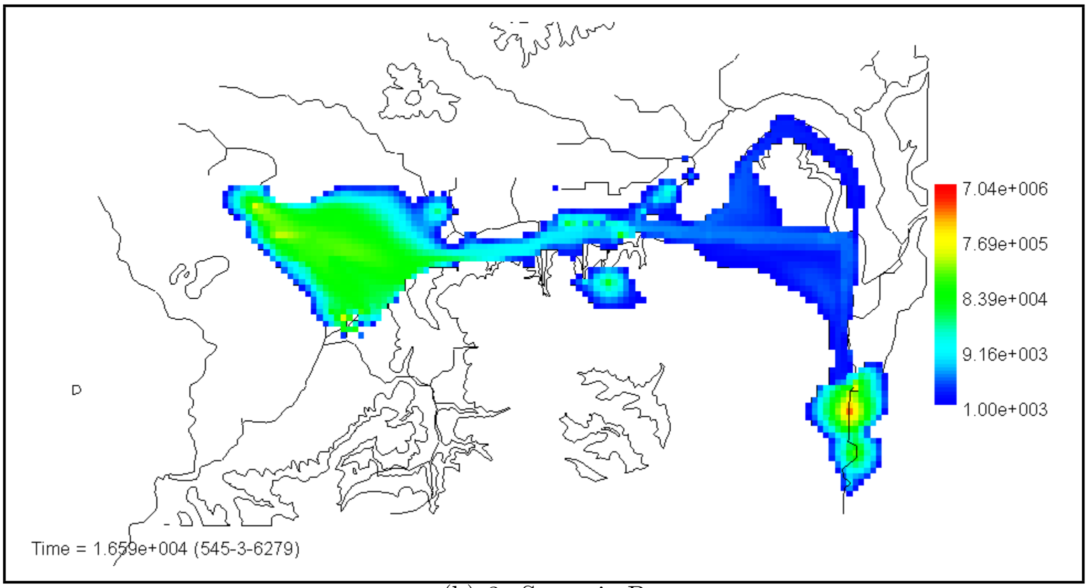


(d) Lynchmill Spring

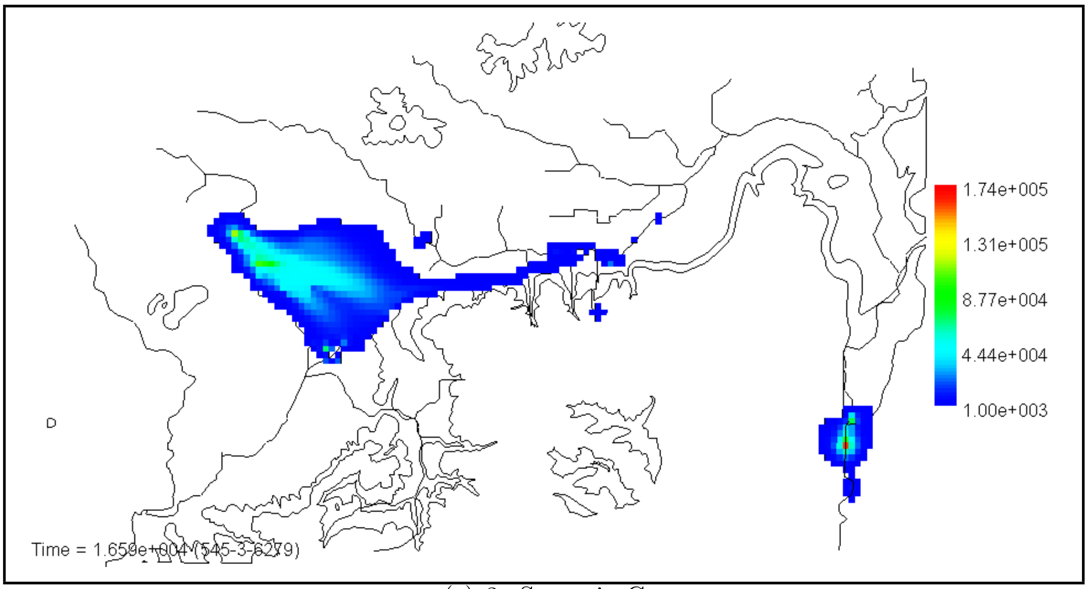
Figure 8.14: Simulations of bromate transport (BST6) using the modified source terms of (Fitzpatrick, 2010) at locations in the Lee Valley



(a) 3×Scenario A



(b) 3×Scenario B



(c) 3×Scenario C

Figure 8.15: Comparative spatial distributions of the plumes resulting from model representation BST6 using the modified source scenarios of Fitzpatrick (2010) for Summer 2010, the shaded plume is at concentrations $\geq 1000 \mu g/m^3$ ($1 \mu g/l$)

Analysis of time-varying spatial distributions indicates that simulated transport of bromate to the Lee Valley via the karst system is highly seasonal, reflecting pulses of bromate transport through the karst zone during summer months when the diluting recharge to the karst system via the swallow hole inputs is reduced. This seasonal response process is illustrated in Figure 8.16.

The seasonal influence causes changes in groundwater flow direction in the Hatfield area at the start of the main recharge period from October to December with additional dilution and flow from the Water End area together with drawdown from abstractions at Hatfield PWS, Roestock PWS and Tyttenhanger PWS (which are all inferred, and modelled as connected to the karst system). This causes part of the bromate plume to be locally redirected south west of Hatfield and impact upon Roestock and Tyttenhanger via a trough-like area of drawdown inferred to be a possible conduit (see section 4.2.2.5) as indicated in figure 8.17. Although concentrations of the simluated magnitude have never been observed at either location, sporadic low concentrations ($\leq 3\mu$g/l) of bromate have been observed at both Tyttenhanger PWS and Roestock PWS. If they are connected to the karst system, the model representation might be indicative of the mechanism by which such breakthroughs could have occurred.

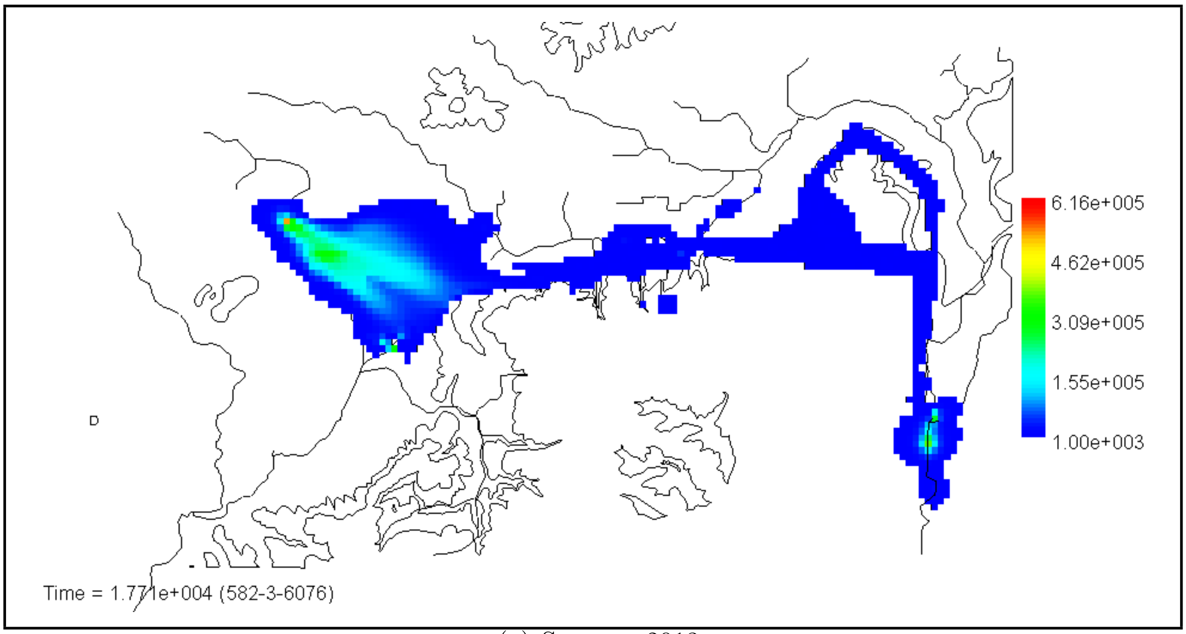
The model indicates two anomalous regions that result either from flow stagnation points or a proportion of the simulated bromate being trapped in low permeability zone (such as in Chalk beneath the London Clay). One of these zones is located almost directly beneath the village of Essendon on the fringes of the Karst zone and appears to result as an artifact of lateral dispersion from the karst zone into a region of slow moving groundwater.

The other zone, located at the southern end of the Lee Valley appears to be a stagnation point resulting from the model geometry. A piezometric low point is located at the centre of this point allow bromate to disperse into the cell, causing it to accumulate mass, but limited variation in heads in the area, partially constrained by the nearby general head boundary means than there is rarely a sufficient hydraulic gradient to allow mass to move by advection out of the cell, although some limited dispersion occurs to surrounding cells.

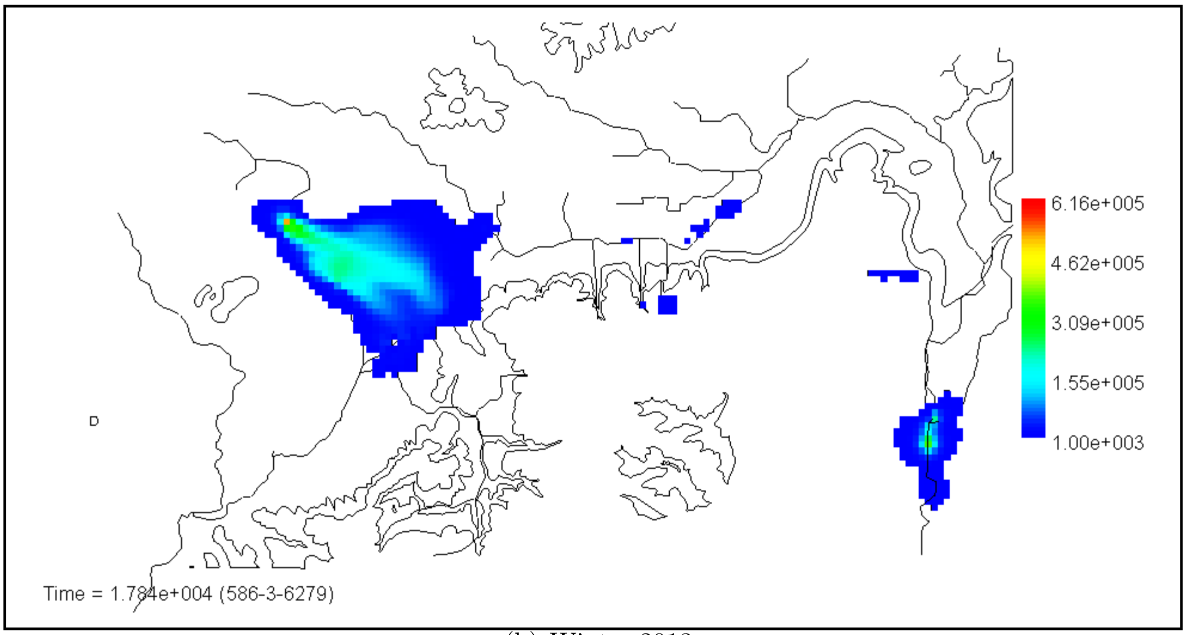
Turnford PWS, the nearest observation point, is located upgradient of this stagnation point and is outside the surrounding halo of dispersed bromate mass, simulations of concentrations at this location do not appear to have been affected by the stagnation point.

8.5 Discussion

The results presented in Figures 8.13, 8.14 and 8.15 indicate that concentrations in reasonable agreement with observations can be simulated using increased bro-

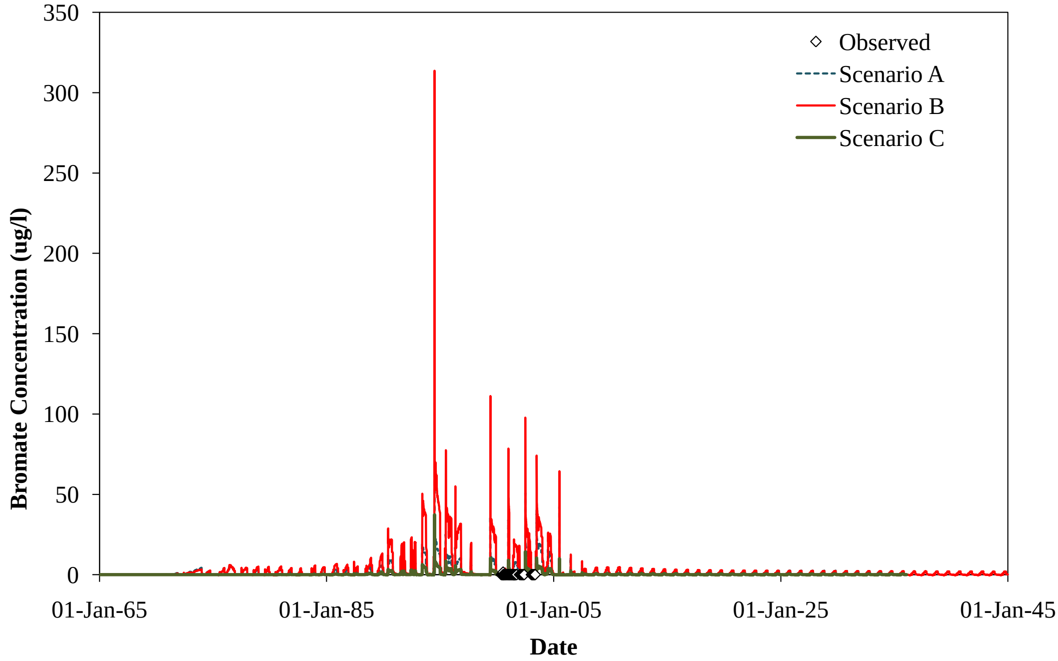


(a) Summer 2013

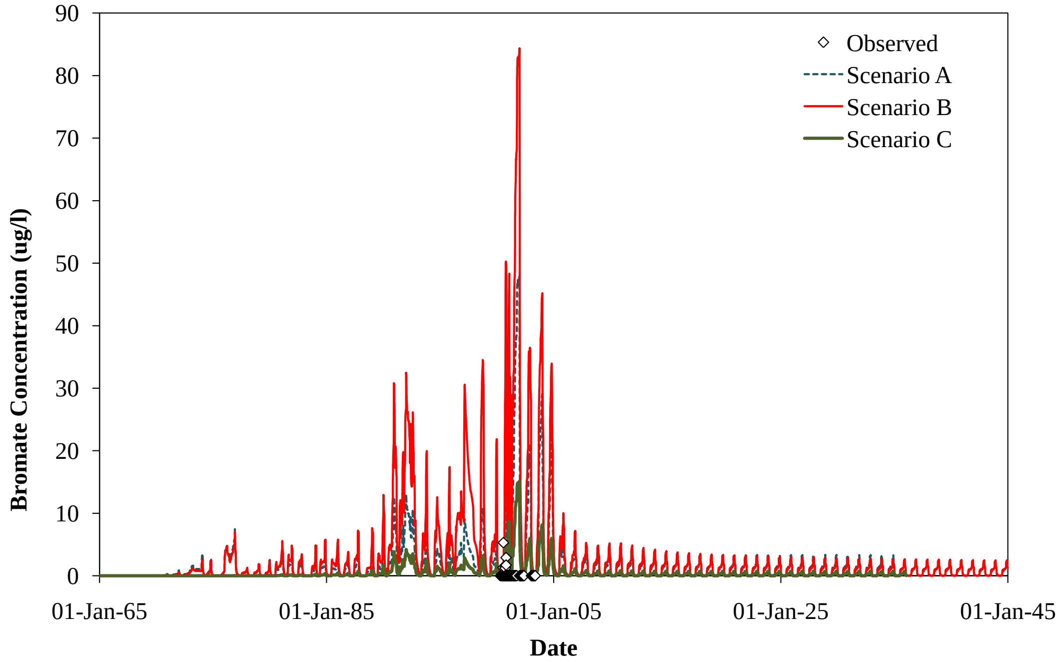


(b) Winter 2013

Figure 8.16: Strong seasonal response of the bromate plume (Scenario B) in the karst EPM zone reflecting dilution of bromate laden water by recharge to the Mymmshall Brook and Palaeocene Feather Edge swallow holes. Concentrations are in $\mu g/m^3$ (Divide by 1000 for $\mu g/l$).



(a) Roestock PWS



(b) Tyttenhanger PWS

Figure 8.17: Sporadic seasonal (Late summer, early autumn) breakthroughs to Tyttenhanger PWS and Roestock PWS occur because of changing flow directions in the Hatfield area resulting from reduced recharge to the modelled Karst zone

mate source terms. Spatial distribution plots presented in Figure 8.15 indicate that the model produces a relatively stable "plume" in the Vale of St Albans area after approximately 10 years of bromate input. Breakthrough to the Lee Valley occurs shortly afterwards due to faster transport within the karst system, and is strongly seasonal. Additionally, the magnitude and timing of the seasonal dilution are approximately correct, particularly at Nashes Farm, Hatfield PWS, Essendon PWS and to some extent Lynchmill Spring. However, the general form, timing and magnitude of the simulated bromate concentrations highlight that there are areas of major uncertainty that limit the effectiveness and confidence in the modelling as a predictive tool using the currently available data. These main uncertainties are:

- The description of the source term and its implementation in the model
- The limited period of observation data in relation to the likely duration of the bromate contamination and especially with respect to the timing of the simulated breakthroughs
- Uncertainty in the extent to which the chalk matrix has become contaminated (i.e. lack of empirical observations of porewater bromate concentrations) and detailed parameterisation of that process
- Deficiencies in the model representation of both dual porosity and karstic transport, and the transfers between them.

The source term has been developed based upon 3 possible interpretations, consistent with the available data for bromate and bromide at the source zone. The model simulations have indicated that Scenario B, with the highest flux occurring due to the 1983-1987 recharge pulse, gives the best fit to observed data. However, the initial simulations have suggested that this source term as described by (Fitzpatrick, 2010) is underestimated; an increase in the source term by a factor of 3 enables observed concentrations to be more closely reproduced. Scoping calculations indicate that an increased mass flux could be accounted for by a relatively small daily volume of bromate discharge to the aquifer. An even higher mass flux, as might result from a catastrophic discharge, could also account for observed concentrations.

It has also been demonstrated that the model can replicate observations using a constant concentration source of 5000μg/l which is approximately equivalent to a mass input flux of 12kg/day. Although such a source is unrealistic in a general sense, it follows that for the model to be able to reproduce observed concentrations for the period 2000-2009, the mass flux need only have occurred at that rate or higher for a similar period of time. If dual porosity attenuation and/or mechanical dispersion are considered, then a larger mass flux over a smaller period of time could also account for observed concentrations. The available monitoring data covers only 9 years for bromate, slightly longer for bromide, so compared to the potential lifetime of the contamination event (perhaps several decades) there is significant uncertainty with regard to the exact timing and magnitude of contaminant release, how that relates to what is observed at monitoring points and by implication, what is modelled.

If the presently observed concentrations are as a result of the 1983-1987 recharge pulse then transport of this pulse through the Vale of St Albans has not been controlled by rapid flows in a karst network. For the 1985 peak mass flux to be associated with peak concentrations in July 2005 (a 20 year travel time) average velocity over the distance of approximately 6km from Sandridge to Hatfield would be at an average advective velocity of 0.8m/day. This agrees well with the Darcy velocities achieved by the dilution testing of (Fitzpatrick, 2010) for the non karstic fracture system. The implication is that the stability of the bromate "plume" as observed over the 2000-2009 monitoring period occurs as a result of the bulk of transport within the Vale of St Albans being within a non-karstic dual porosity matrix-fracture system.

The apparent rising trend from 2000-2005, which although could be due to progression of the recharge pulse, can also be attributed to the a change in flow conditions caused by the cessation of abstractions at Hatfield PWS (e.g Buckle, 2002; Hay and Buckle, 2006) in November 2000, a trend which has since been reversed by adoption of scavenge pumping at Hatfield in July 2005. This has caused observed concentrations to peak in 2005 and reduced concentrations thereafter, which is likely to be a result of returning to conditions similar to those that existed prior to 2000.

This does not discount the possibility that rapid flow paths of limited attenuation, as inferred from the tracer testing, do exist in Vale of St Albans. In addition to the tracer evidence, small conduits have been observed in boreholes in the northern part of St Albans (CL:AIRE, 2002). Unexplained short term (days) variations in concentrations at Hatfield PWS could also be due to the influence of karstic pathways. Minor conduits embedded within the dominant fracture system with only partial interaction with the main bromate-bearing fractures could influence observations via dilution or supply of additional bromate. The conduit pulses might be strongly influenced by recharge events or local variations in water levels, for example due to abstractions. Such a scenario could also provide an explanation for the rapid transport but low recovery of the $MS2$ and $\Phi X172$ tracer via a limited conduit system, with the majority of bacteriophage being lost to the non karstic fractures, consistent with the conceptual model and findings of Maurice et al. (2006) and Maurice (2008). Observed concentrations in the area of Hatfield occur could be the result of superposition of the diffusive double porosity dominated transport with pulses of flow through a limited network of conduits.

The above discussion assumes that the model is an adequate approximation of the aquifer which it represents. However, an equivalent porous media model cannot represent both the conduit and fracture systems simultaneously in the same grid space as occurs in reality. Model cells must either be an EPM of the Karst conduits or an EPM of the non-karstic fracture system. The representation of karst within the Vale of St Albans as a westward extension of the main karstic zone is only a very crude representation of the likely reality; the best replication of the Vale of St Albans transport in MODFLOW and MT3D-MS is achieved using a non-karst, dual porosity approximation.

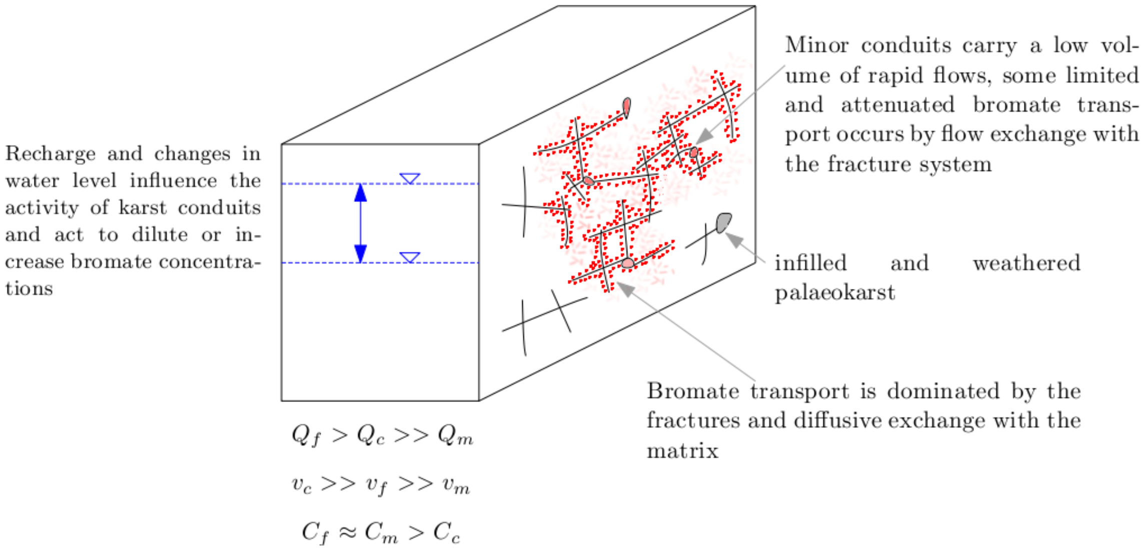
Conversely, the model approximation of the majority of transport east of Hatfield being dominated by an EPM representing karst transport, is limited by the exclusion of the double porosity matrix-fracture system and is illustrated by the simulations of transport to locations which receive a large karst component such as Essendon PWS, Arkley Hole or Lynchmill Spring in Figure 8.15. The model behaviour does approximate transport in the conduit system, which during summer months is maintained by low flows to the swallow holes and contributions from the fractured chalk to saturated conduits. During winter months increased recharge dilutes bromate concentrations, thought to be the cause of the strong seasonal relationship with soil moisture deficit observed at Essendon PWS (Lytton, 2005). However, the simulated behaviour does does not incorporate the contribution of the double porosity matrix-fracture system in the karst zone and its role in maintaining bromate concentrations during winter months by diffusive exchange and in buffering the change in flow directions due to recharge. These discrepancies in the model representation are illustrated in Figure 8.18

8.5.1 Possible Long Term Evolution of the Bromate Contamination

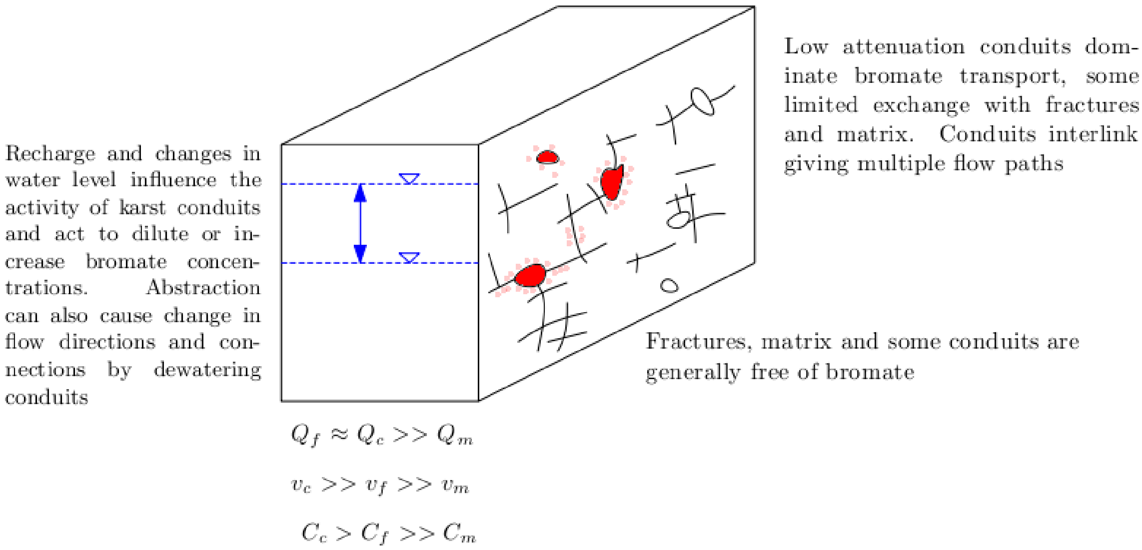
The numerous areas of uncertainty limit the confidence with which any long term predictions can be made, particularly when considered with regard to the relatively short period of available observations, and particularly the lack of any porewater data with which to constrain the influence of the chalk matrix. A further complication is that the MT3D-MS first order approximation of dual domain transport processes does not simulate back diffusion from the immobile zone and hence the role of the Chalk matrix in extending the duration of contamination events is neglected.

The modelling period extends from 1965-2045, and both observation and modelling data suggest a relatively stable situation for the Vale of St Albans which is strongly influenced by extensive matrix porewater contamination and double porosity diffusive exchange, but for establishing trends the Hatfield area and locations downgradient, the available data are complicated by the influence of changing abstraction at Hatfield PWS and its resulting impact on karstic flow paths.

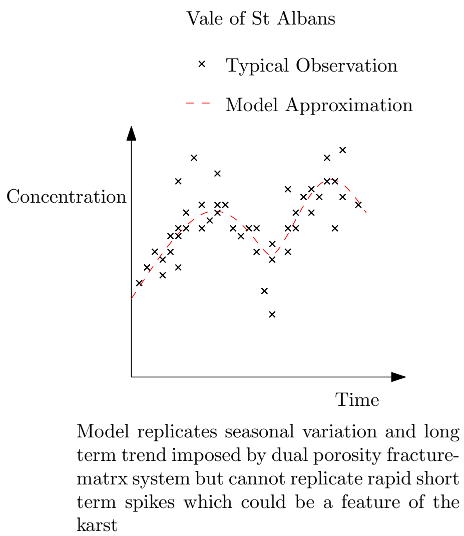
The situation as modelled suggests that current observations are the result of the passage of the 1983-1987 high concentration recharge pulse through the aquifer. This peak is predicted to decline to a plateau and then to tail off very slowly over



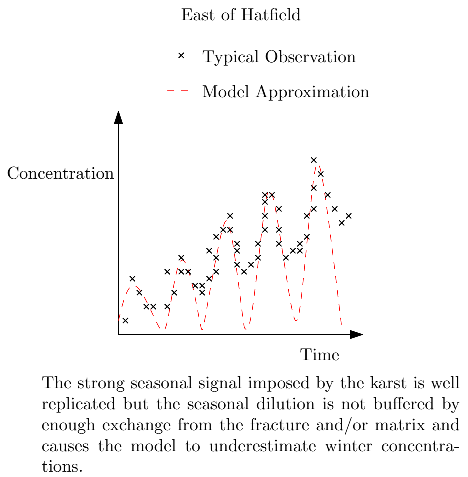
(a) Vale of St Albans. An EPM representing the non-karstic fracture and matrix system provides the best approximation of transport processes, and hence cannot replicate the rapid transport processes imposed by the karst



(b) East of Hatfield. An EPM representing the karst conduit system provides the best approximation of transport processes but cannot replicate the buffering of concentrations by the matrix and fracture system



(c) Vale of St Albans



(d) East of Hatfield

Figure 8.18: Discrepancies between an idealised reality and the model EPM representation of flow and transport in both the Vale of St Albans and the karst dominated zone east of Hatfield

the remainder of the modelling period (i.e. at least until 2045) as a result of the dual domain attenuation and sustained low mass flux from the contaminant source.

At Nashes Farm, the recharge pulse arising from site clearance between 1983-87 is simulated to have already passed, and concentrations have reached a near plateau level between $100 - 200\mu$g/l. These are predicted to gradually fall reaching approximately 50μg/l by 2045. Observed concentrations are presently in the region of $1000 - 2000\mu$g/l. Scaling the model output to these concentrations, suggests concentrations could persist above 500μg/l at Nashes Farm for at least the next 30 years. At Hatfield PWS the model indicates that current observations reflect the late stage passing of the recharge pulse and that concentrations are gradually decreasing. However the rate of decrease is slowing and concentrations in range of $10 - 50\mu$g/l persist until at least 2045.

The model predicts that a "plume" at moderately high concentrations in excess of the drinking water standards will persist within the Vale of St Albans for the remainder of the modelling period, despite the passing of the 1983-1987 recharge pulse.

For Essendon PWS and locations within the Lee Valley, the model suggests that bromate concentrations will decline below drinking water standards once the high mass flux associated with the 1983-1987 recharge pulse has dissipated by 2020. However, periodic seasonal pulses of several μg/l still occur at Essendon and Arkley Hole until 2045 so monitoring and continuing vigilance will be necessary. Concentrations, typically $\leq 1\mu$g/l occur at locations in the Lee Valley for the remainder of the modelling period and are strongly influenced by karstic seasonal dilution.

The model has proven effective at reproducing observed order of magnitude of bromate concentrations with a constant concentration source of 5000μg/l but long term predictions cannot be made from this equilibrium source term. If the actual bromate mass flux from St Leonard's court is well approximated by a 5000μg/l constant concentration for a period of at least 5 to 10 years, then maximum concentrations should not significantly exceed those recorded during the period 2000-2005 when Hatfield PWS abstraction was suspended. This prediction cannot be validated without further investigation of the historical bromate mass flux from St Leonard's Court.

The simulated three-fold increase over the mass fluxes of Fitzpatrick (2010) has still proven to be insufficient at replicating the magnitude of observed concentrations, particularly for Lee Valley locations, which suggests that mass fluxes may have been even greater. Application of the CXTFIT advection dispersion model (Toride et al., 1995) (Appendix E) to estimate an equivalent source concentration for the duration of the 1983-1987 recharge pulse by fitting of a dual domain model suggests that a sustained source concentration equivalent to several 1000μg/l can simulate concentrations of appropriate magnitude.

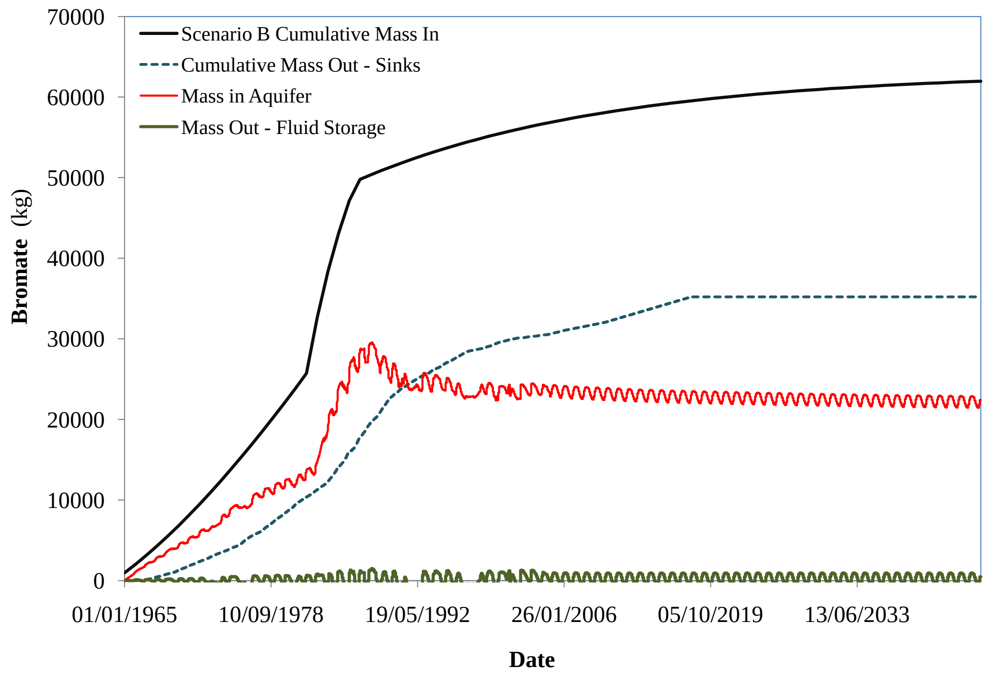


Figure 8.19: Mass Balance with time for the predictive model

8.5.2 Bromate Mass Balance

The model mass balance for the modified bromate source Scenario B is presented in Figure 8.5.2. The greatest mass change occurs between 1983 and 1992 due to the input of the recharge pulse. Approximately one third of the total mass input (23 tonnes) remains in the aquifer beyond 1992 with mass removed at sinks (i.e. wells and other boundaries) being accounting for the mobile part of recharge pulse up to 2017. When the time series and spatial data are considered against the mass balance it appears that the majority of the bromate mass is retained within the Vale of St Albans and is the cause of persistent bromate concentrations above Drinking water standards at Nashes Farm and Hatfield. Ground water in the Vale of St Albans is moving very slowly so does reach the larger abstraction wells such as those in the Lee Valley at sufficient concentrations to cause a noticeable reduction in the mass balance by this time.

The stagnation point at the southern end of the River Lee reaches a concentration of approximately $460\mu g/l$ by the end of the modelling period in 2045. taking the dimensions of the cell as 200 x 200 x 25m ($1000000m^3$) and assuming the porosity (0.38) is fully saturated, the cell accounts for approximately $1.74 \times 10^8 \mu g$ ($174g$) of bromate. Expanding the affected volume to all affected adjacent grid cells, which covers an area of approximately 6km^2 much of which is at significantly lower concentration. The maximum mass estimate for the total affected stagnant zone is 25kg and therefore does not account for the 23 tonnes of bromate remaining in the model in 2045.

8.5.3 Effectiveness of a Scavenging Well

For scavenge pumping to be effective, the fracture porosity should have a high degree of connectivity and hydraulic conductivity across the width of the plume. A successful scavenge pumping well must be connected to, or able to capture a significant volume of upgradient contaminant and also be connected to, or able to influence connections or flows to the downgradient sources which it is acting to protect. Whilst this generally applies for homogeneous porous media it does not necessarily follow in highly heterogeneous aquifers such as the Chalk. The only location for which this degree of connectivity has been proven in the Hertfordshire Chalk is Hatfield PWS which probably exploits its connection to the karst system to influence down-gradient concentrations.

Establishing a direct link to the karst system, either at a location where such flows are developed along the Palaeocene Feather Edge or a connection to the karstic routes developed within the Vale of St Albans should prove the most effective method of scavenge pumping, particularly for protecting the Lee Valley abstraction wells. However, the probability of intercepting a karst conduit in any specific drilled borehole is extremely low (Worthington and Ford, 2009) and additional field investigations are be required within the Vale of St Albans to better locate the main bromate flow paths in plan and in vertical profile.

The distribution of contaminant mass is important in determining the effectiveness of a scavenge pumping borehole, in particular the extent of its invasion of the matrix pore space as a result of diffusive exchange. This is particularly so when considering the limited downgradient dimension of the well capture zone illustrated in Figure 8.3. The most effective location for a scavenge pumping well would be downgradient of the centre of mass of contamination.

More precise knowledge of the distribution of the bromate contamination than is currently available is required and in particular the extent to which matrix porewater within and adjacent to the Vale of St Albans has become contaminated. Currently this is a major uncertainty since only limited data are available for matrix porewater directly beneath St Leonard's Court and no data are available for any other location. This information can only be determined with certainty from a cored borehole from which porewater abstraction can be made and it is likely to have a significant bearing on the effectiveness and location of any scavenge pumping well. The spatial distribution of bromate and the overall magnitude of bromate concentrations within the Vale of St Albans (see section 2.1) have remained relatively stable since monitoring began which implies buffering by extensive porewater contamination. If this is the case, the effectiveness of scavenging may be limited but this should be determined by further investigation.

If it is assumed that the source term and adopted dual porosity parameters from the modelling are approximately correct, the model simulations suggest that a new scavenge pumping borehole may be of limited significance since the majority of contaminant mass (resulting from the 1983-1987 recharge pulse) has already passed through the aquifer from Sandridge to the River Lee. However, scavenge pumping may still be effective against the persistent contamination released from porewater storage near the bromate source and within the Vale of St Albans.

Predictive simulations have hitherto assumed a “do nothing” approach in which the current pumping regime in the aquifer is maintained. However, an alternative possibility for the near-source scavenge pumping were considered.

- A near-source scavenge pumping borehole was added to the model at the approximate location of the Nashes Farm observation borehole/private abstraction (NGR TL 518025 209657) at a rate of 5Ml/day starting in January 2010 until the end of the simulation period

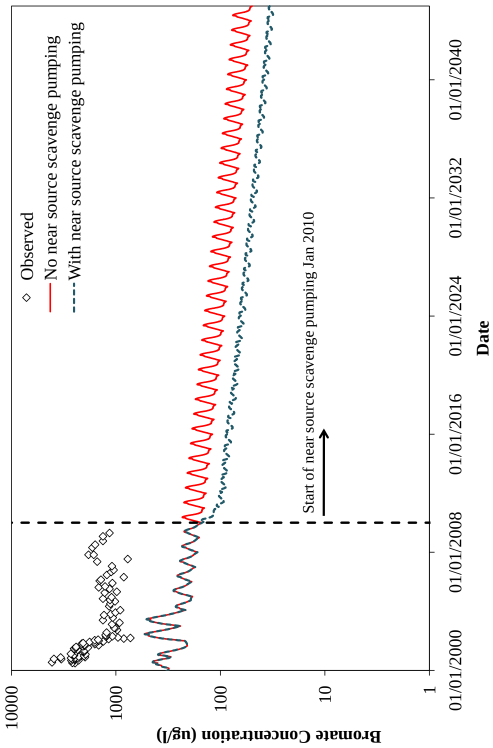
- Near Source scavenge pumping did not occur

The model results of the “do nothing” and near source scavenge pumping future are presented in Figure 8.20

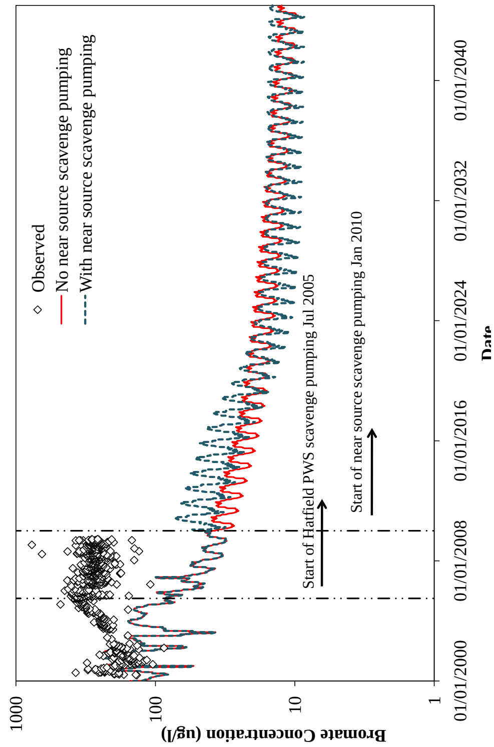
Scavenge pumping results in a 30-40% reduction in bromate concentration at the location of the scavenge pumping well after 1 year of abstraction and remains similarly effective until the end of the modelling period in 2045. At Hatfield PWS, simulated bromate concentrations rise as a result of the switch off of the Hatfield PWS scavenging in 2010 and remain at high concentrations for a period of 11 years reflecting the time required for upgradient scavenging to take effect. Subsequently, concentrations return to a similar level then under Hatfield PWS scavenging operations, suggesting that the near source abstraction may ultimately be of similar effectiveness to Hatfield PWS.

The 11 year relative rise in concentration resulting from the cessation of abstraction at Hatfield PWS also occurs at Essendon PWS, Arkley Hole and Lynchmill Spring. At Essendon the near source scavenge pumping shortens the duration at which concentrations remain above $1\mu g/l$ by approximately 8 years but does not appear to have a significant impact on the duration or magnitude of concentrations at Arkley Hole and Lynchmill Spring.

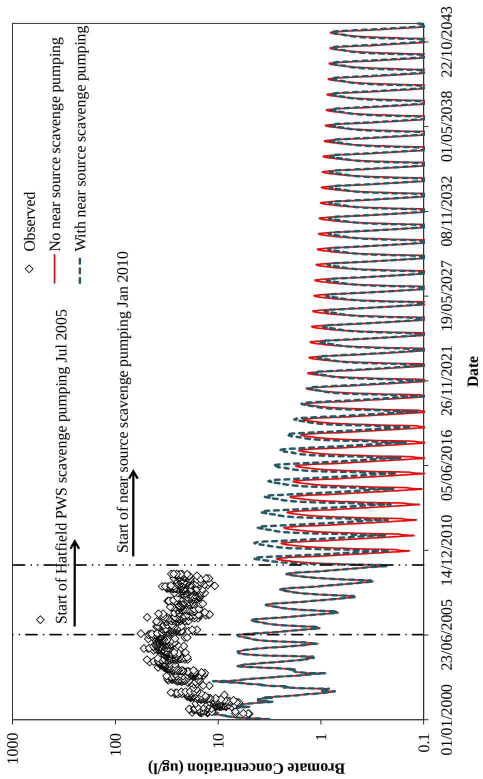
A possible alternative scavenging location that could also be effective in protecting the Lee Valley in the short term is at Essendon PWS, this has also been shown to have a strong connection to the karst system and showed probable breakthroughs all three tracers. Concentrations at Essendon have also been statistically linked with those at Hoddesdon, Broxbourne and Turnford (Robinson and Buckle, 2004). Due to the shortfall resulting from the removal of Hatfield PWS from supply, Essendon PWS has been in operation nearly constantly since 2000. It is possible that if abstraction at Essendon PWS was discontinued for a prolonged period, concentrations at the Lee Valley may increase as a result.



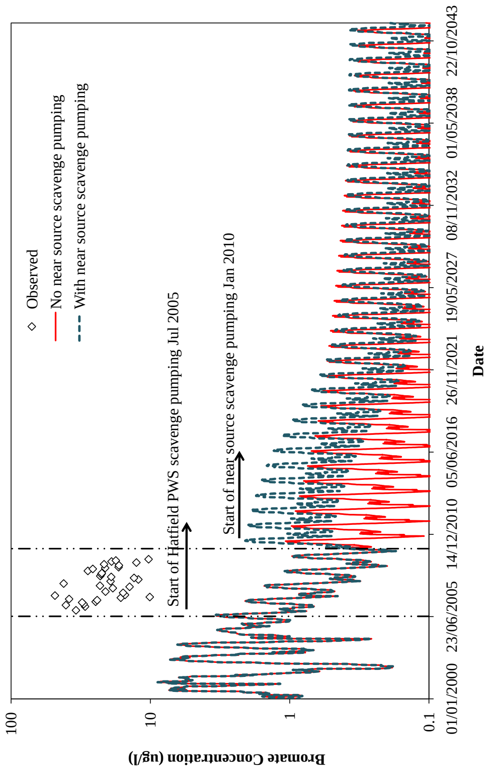
(a) Nashes Farm Scavenge Pumping Well



(b) Hatfield PWS



(c) Essendon PWS



(d) Lynchmill Spring

Figure 8.20: Responses to scavenge pumping at Nashes Farm and Hatfield PWS

Although the absolute magnitudes are incorrect, the model does replicate the style of response to changes in abstraction at Hatfield PWS relatively well indicating reduced concentrations at downgradient locations during abstraction periods and a relative rise in concentration during switch off periods. This lends further confidence that the model is able to replicate crucial features of the karst flow system. However, until uncertainties regarding source concentrations and dual porosity are resolved the predictive power of the model is limited.

8.5.4 Summary

The model simulations are able to replicate many characteristic features of the bromate transport regime:

- A stable bromate plume of approximately correct geometry in the Vale of St Albans
- Rapid transport via the karst system to downgradient locations in the Lee Valley
- A strong summer seasonal trend of high concentrations in the karst zone
- Concentrations of similar magnitude to observations at many locations
- The magnitude of seasonal variations in observation concentrations is also well reproduced

Travel times indicate that transport within the Vale of St Albans is dominated by dual porosity fracture-matrix diffuse exchange and that karst development is probably limited to low volumetric flux, highly attenuating but rapid flow paths.

Additional inferences resulting from the model simulations are that the bromate source term could be much larger (by a factor of 3 or 4) than was inferred by Fitzpatrick (2010). Modelling also suggests that present day observation concentrations could be accounted for by a source with constant concentration of $5000\mu g/l$ or mass flux of approximately $12kg/day$ for a period of 9 years

Long term modelling suggests concentrations may remain at hazardous concentrations with respect to drinking water standards within the Vale of St Albans for at least the next 30 years and potentially much longer. Furthermore, the existence of the low attenuation karst system implies that as long as hazardous concentrations exist within the Vale of St Albans and Hatfield area, there is potential for hazardous concentrations to occur sporadically at Lee Valley locations.

Simulations of scavenge pumping at a near source location have been shown to be of relatively limited effect since the simulations have implied that the main peak of concentration resulting from an inferred high mass flux between 1983 and 1987 has already passed most observation points.

However, there remain significant uncertainties with respect to the available data and modelling approach which must be resolved by additional field investigations in order to increase confidence in the above findings.

- There is little knowledge of the extent of matrix contamination that has occurred, particularly at Sandridge but also in the Vale of St Albans. As a result there is no data with which to calibrate the distribution of aquifer mass

- Limited bromate data for the source site limit confidence in the source terms, which has a significant impact on the model simulations

- Limitations in the representation of matrix-fracture and fracture-conduit exchange in the equivalent porous media modelling approach restrict the models ability to replicate these transport processes, and the interactions between them

- These uncertainties, coupled with a limited duration of observation data at receptors, make direct comparison of simulated concentrations with available data difficult

Given the above discussion, errors of ± 10 years in the travel time and contaminant release time from the source, and of at least a factor of three and perhaps up to an order of magnitude in contaminant flux, might be realistic. Simulated concentrations are well within these error envelopes when compared to the observation data.

To improve the model calibration, in terms of understanding the timing and magnitude of source term and the transport processes at work, one or more cored boreholes are required. The greatest need is within the Vale of St Albans where both the empirical field data and the modelling imply that diffusive dual porosity exchange is the dominant mechanism controlling bromate concentrations.

Only with this data could a proper estimate of the distribution of bromate mass in the aquifer be made. This would also yield essential information with regard to the source flux, dual porosity transport parameters and the likely effectiveness and location of a scavenge pumping well. These data could be used to calibrate a fully diffusive dual porosity model of the fracture system which coupled with the quantitative parameterisation of the karst system and a suitable karstic model, whether the EPM approximation used in this approach or a more specifically karstic model (such as a finite element type approach) would significantly increase the confidence in long term predictions. Fitzpatrick (2010) is developing a "multiple-analytical-pathways" (MAP) approach that will begin to address some of these issues incorporating a fully diffusive representation of dual porosity transport in combination with the karst characterisation and aquifer flowpaths derived from this modelling approach. This will be able to provide predictions of dual porosity behaviour that can be validated against future porewater data.

Chapter 9

Conclusions

In considering the implications of the work presented in this thesis it is useful to consider the findings against the initial research objectives as defined in Chapter 1 which are repeated below for convenience.

- Re-evaluate previous work on the aquifer and the bromate problem in the context of the karst flow system
- Investigate the karstic system through a catchment scale tracer test, analysis of historical tracer tests and other relevant data
- Derive a new and improved conceptual understanding of the hydrogeological function of the Hertfordshire karst and consider the findings in terms of field observations.
- Appropriately incorporate the conceptual understanding of the Hertfordshire karst system into a range of catchment scale groundwater flow and transport models using different aquifer representations that can be calibrated and validated against available data
- Provide predictive envelopes of the future evolution of bromate at points of interest in the aquifer and under different potential future scenarios/stress conditions

Although significant uncertainties remain with regard to the precise location, dimensions and flow volumes within the chalk karst the principal aim of developing an improved conceptual understanding of the Hertfordshire karst has been achieved and represents an improvement on the previously established concept that the karst represented a series of radiating fractures or flow paths from Water End to the Lee Valley. Tracer tests and the extent of surface karst have indicated that the distributive karst network extends along and adjacent to the Palaeocene feather edge from the Mymmshall Brook to the Lee Valley. For the first time, understanding of the Hertfordshire karst has been integrated with empirical observations of its hydrogeological behaviour, consistent with the geological history of the whole catchment.

The tracer tests have indicated some of the longest flow paths and highest tracer recoveries and longest flow paths ever recorded in the karstic chalk, attesting to the limited attenuation capacity of the network. It is the influence of this karst that appears to be a major contributing factor to the occurrence of bromate at locations in the Lee Valley.

The tracer tests have also revealed that rapid karstic flows are more widely distributed throughout the aquifer than was previously thought, possibly extending into the Vale of St Albans away from the main surface karst. It may extend even further north west, being associated with the Clay-with-Flints deposits present on the Chalk Dip Slope. The tracer interpretation supports recent work by (Maurice et al., 2006; Maurice, 2008) and Worthington (2003) which has suggested that karst and solution enhancement of the aquifer is more common in Chalk than previously established. However, despite the identification of karst development in the Vale of St Albans, solute transport in its vicinity appears to be overwhelmingly dominated by dual porosity transport in the fracture and matrix system.

The new conceptual understanding, specifically the inferred geometry of karstic flows and transport parameters derived from analytical modelling of the tracer test data, have been incorporated into a a spatially distributed groundwater flow and transport model. The model is able to reproduce aquifer heads and flows. Through use of MODPATH the model can approximate the principal karstic flow routes, and through use of solute transport package, MT3D-MS, the tracer test breakthrough curves can be simulated within a model of the regional groundwater flow system. The final calibrated transport parameters in the spatially distributed model are also consistent with the estimated range of parameters derived from the tracer tests. That the modelling is able to replicate the tracer behaviour and in particular simulate transport to the Lee Valley, an area where previous models have proven inadequate, lends confidence to the use of the model as a predictive tool for simulating the behaviour of bromate.

The final research objective has only been partially met. Application of the model to the bromate problem has shown that the transport processes at work are also strongly influenced by dual porosity attenuation, which is poorly constrained given the present lack of data on porewater contamination by bromate. The MODFLOW family of models approximates matrix diffusion as a one-way partition and back diffusion from the Chalk matrix is not simulated. Although the model is able to approximately simulate bromate concentrations at observation points under certain input conditions, limitations of the model in representing dual porosity and karstic transport in the same grid space, coupled with uncertainties concerning the bromate source and the contamination of pore water, limit confidence in the long term predictive power of the model. It is unlikely that these issues can be resolved until sufficient data are available to develop an improved representation of an effectively triple porosity Chalk aquifer containing discrete representations of the matrix, fractures and conduits, and improved modelling approaches are developed.

9.1 Wider Implications

9.1.1 The Chalk Hydrostratigraphy and Bromate

The lithostratigraphy and structural features of the Chalk aquifer have been shown elsewhere in the United Kingdom to influence the aquifer properties that influence both flow and transport. In particular, Watson (2004) has shown that dual porosity diffusive exchange is strongly dependent upon the fracture and matrix properties specific to stratigraphic units.

The identification of the Hertfordshire Chalk stratigraphy using geophysical logging (Woods and Aldiss, 2004; Randle, 2005) has allowed a structural analysis of that data in this study. This has indicated that the New Pit, Lewes Nodular and Seaford Chalk Formations are the most important aquifer units in the affected area of Hertfordshire, with the significance of the New Pit diminishing in favour of the Seaford Chalk from west to east.

Although the spatial distribution of the Chalk formations has been delineated, no clear correlation can be made between the occurrence of bromate and the variation in lithostratigraphy across the catchment. The distribution of bromate cuts across all three of the main formations present and although it has been speculated that the Chalk Rock member and the hardgrounds of the Lewes Nodular Chalk could be principal flow horizons with reduced dual porosity attenuation due to their low primary porosity, this is not evident in the available field data.

Given the relative absence of data for the Hertfordshire Chalk a generic parameterisation of the likely fracture properties has been derived from empirical data from adjacent areas. At this time there is little justification in using the generic data in anything but an indicative sense. A critical area of uncertainty for this hydrostratigraphic approach is the lack of data concerning vertical variation in hydraulic properties (perhaps arising from the stratigraphy) and hydrochemistry in Hertfordshire and how these relate to the transport and distribution of bromate. This limited knowledge of the vertical dimensionality of the problem partially explains why at present only a single layer model approach can be justified as the most parsimonious approach at this time. A single layer approach is reasonable given the extensive lateral distribution of contamination, extending over tens of kilometers compared to the likely effective thickness of the aquifer of several tens to a few hundred metres.

As with bromate, the occurrence of karst in Hertfordshire cannot be clearly correlated with the Chalk lithostratigraphy. The majority of surface karst features (including Arkley Hole, Chadwell and Lynchmill Springs) occur above the outcrop of the Seaford Chalk Formation. Head data suggest that the elevation of the water table also occurs within the Seaford Chalk east of Hatfield. In the Vale of St Albans most the of the effective aquifer from Sandridge to the Lee Valley, in addition to the Mymmshall Brook catchment including the Water End swallow holes, occurs within the Lewes Nodular Chalk. Tracing experiments from Water End also suggest that the Lewes Nodular Chalk may be important, since Hatfield PWS and Essendon PWS are developed almost entirely within the formation, as are most of the Lee Valley wells. The absence of Seaford Chalk in Vale of St Albans implies where karst development occurs in the Vale, it is within the Lewes Nodular Chalk. Only Hoddesdon PWS and Turnford PWS contain extensive thicknesses of Seaford Chalk in their uncased sections.

Although there is potential to develop a lithostratigraphic aquifer framework for Hertfordshire the distribution of bromate and karstic flows together suggest that the aquifer structure, geomorphological history and the resulting distribution of karst features appear to be dominant controls governing the spatial distribution of bromate and these features appear to be imposed on the Chalk regardless of stratigraphy.

Optical televiewer and closed circuit television inspection of non-screened deep boreholes (of which there are relatively few) would be extremely useful. This would allow fracture styles, spacings and apertures to be estimated and considered with the lithostratigraphy, as has been achieved in other locations. New investigation boreholes would allow core to be retrieved, further constraining the stratigraphy and allowing direct measurement of porosity, fracture spacing and pore water chemistry. Packer-testing and additional dilution tracer tests could also be carried out to delineate flowing horizons and their properties.

Optical borehole logging and/or core retrieval would also allow investigation of the style, size type and distribution of karst development in the subsurface. Such a technique was used successfully in the Berkshire Chalk by Maurice (2008) to show conduit development (up to 15cm in diameter) occurring at least 74m below ground level and solution enlargement of fractures at greater depths.

9.2 Chalk Karst

The existence of the Hertfordshire karst has been known for centuries, and tracer testing by Harold (1937) established a rapid, low attenuation connection between the Mymmshall Brook swallow holes and the wells and springs in Lee Valley. A clear link between the karst and the Chalk lithostratigraphy cannot be established. The development of karst in Hertfordshire is closely linked to the structure and geomorphological evolution of Hertfordshire and in particular the role of the Proto-Thames and Vale of St Albans Glaciation in exposing, weathering and controlling surface and subsurface flows.

The existence of karst within the Vale of St Albans supports the hypothesis of Maurice et al. (2006); Maurice (2008) that karst can be present in subsurface Chalk distant from the Palaeocene feather edge and that it need not be related to, nor connected to development of surface karst. Maurice (2008) has speculated that mixing corrosion at fracture intersections could be one possible mechanism by which karst could be formed without aggressive allogenic input from swallow holes.

In Hertfordshire the geomorphological zonation model of (Maurice et al., 2006) does not apply and the geological history of the Vale of St Albans also needs to be considered. Retreat of the Palaeocene escarpment did not occur in the same fashion as Berkshire. The present day Palaeocene escarpment represents the limit of Proto-Thames and glacial erosion. The true escarpment (due to dip slope retreat sense) is still present to the north west of Welwyn Garden City, marked by minor outliers of the Lambeth Group and London Clay. By implication, the Vale of St Albans is still within "Zone 1" as defined by Maurice et al. (2006).

This major difference is expressed in the characteristics of Hertfordshire Chalk karst, compared to that of the Berkshire Chalk. The Chalk lithostratigraphy in Berkshire and Hertfordshire is approximately the same, with Seaford Chalk at ground level overlying Lewes Nodular Chalk in the subsurface (Aldiss et al., 2002, in (Maurice, 2008)). The karst of Berkshire Chalk has been well studied in recent years (Banks et al., 1995; Maurice et al., 2006; Maurice, 2008) and tracer tests have established rapid low attenuation flows from swallow holes to springs over distances of several kilometers, although generally shorter distances than have been proven for Hertfordshire. The direction of flows in Berkshire, and the apparent spring catchments of (Maurice, 2008) appear to be down-dip, or parallel to groundwater and surface water flow directions as inferred from hydraulic head. In Hertfordshire, karstic flow occurs approximately along strike southwest to northeast but still in direction of groundwater head gradients due to the elevation of the North Mymms Recharge mound and the low hydraulic gradients east of Hatfield. The principal difference therefore appears to be in the relative position of surface drainage and land surface elevations. In Berkshire, the Rivers Pang and Lambourn drain south and east down the dip slope of the Chalk, cutting into the Palaeocene and leading to the occurrence of coincident swallow holes and springs. This contrasts with Hertfordshire, where the Vale of St Albans forms a topographic low north and west of the Palaeocene outcrop, promoting surface drainage and groundwater flow and development of permeability anisotropy sub-parallel to the valley axis. Landscape erosion has exposed subsurface conduits and appears to be a factor in the occurrence of springs and in establishing the orientation of karst flows.

The presence of karst within the Chalk aquifer of Hertfordshire and its influence on the evolution of the bromate contamination contrasts with the dual porosity diffusive exchange that dominates solute transport in a similarly extensive contaminant plume in the Tilmanstone valley of Kent. These two cases demonstrate that extensive contamination can develop in the Chalk under more than one set of hydrogeological circumstances. The apparently widespread existence of Chalk karst suggested by this and other studies in areas adjacent to, overlain by, or formerly overlain by the Palaeocene Lambeth Group complicates groundwater protection and assessment of the vulnerability of abstraction wells.

Edmonds (2008) has defined a semi quantitative method for establishing the Chalk aquifer vulnerability in the presence of Chalk karst. Although this method gives indicates the likelihood of subsurface karstic flows and therefore the relative vulnerability of any given location, it does not consider connectivity and transport properties of the karst. For example, whilst the method would likely establish the Hertfordshire Chalk aquifer as vulnerable to karst, it would not identify the specific low attenuation pathways between Water End and the Lee Valley as is necessary in order to define abstraction well catchments and therefore their absolute vulnerability.

Tracer testing is a powerful method for in establishing definite groundwater connections and the flowpath but the ambiguous nature of non-detections are a persistent limitation. The interpretation of tracer results can themselves be non-unique. For example, the conceptual model that arose from the 1930's tracing suggested a set of radiating north-east oriented conduits from Water End to the Lee Valley; re-evaluation of these data and new tracer test data has implied that rapid occur sub-parallel to the Vale of St Albans and Palaeocene feather edge. Consideration of the geological history and structure of the aquifer should always incorporated when considering tracer test results.

The new conceptual understanding presented for the Hertfordshire Chalk karst improves upon previous work in the area, suggesting that karst is more widespread than previously thought and providing the first estimates of the geometry, dimensions and flow and transport properties of the system. Although, the karst plays an essential role in the distribution of bromate to affected locations in the Lee Valley, there is no evidence that karstic flows dominate aquifer processes. The Chalk karst appears to be an efficient distributary system for a moderate flow volume, at least a portion of which contains a high proportion of the bromate mass reaching the Lee Valley. However, both simple water balance and modelling indicate that the majority of groundwater flow occurs within the non-karstic fracture system of the Chalk, in which transport is expected to be dominated by double porosity diffusive exchange.

9.3 Bacteriophage as Groundwater Tracers

Bacteriophage tracing has indicated rapid groundwater flow connections over much larger distances than previously recorded, attesting to both the high sensitivity of the tracers and the limited attenuation of karstic flow paths. Tracer injection at Water End has resulted in much larger recovery than achieved in the comparable investigations of Maurice (2008), whilst the magnitude of breakthroughs from the two borehole injections were comparable to those of (Price et al., 1992). That bacteriophage provide a useful tracer of long distance groundwater transport with a high degree of dilution, and particularly where water quality is a concern, has been reinforced by this study. However, a number of areas of uncertainty still exist and addressing them could improve interpretation of bacteriophage tracing results.

The background presence of a low concentrations of bacteriophage led to additional uncertainty in verifying phage breakthroughs of $\Phi X174$ and $MS2$. This uncertainty could be reduced by improving characterisation of background phage. However, detectable background concentrations were not observed by Maurice et al. (2006) or by Price et al. (1992) despite the latter tracer test occurring in a similar region of aquifer, only 10km to the South west along the strike of the Chalk. Background occurrence of phage may be highly location-specific but given the limited data available it is impossible to draw any general conclusions. The available data suggested that occurrence of the background phage is linked to rainfall and the relative proportion of karstic flow, which could indicate that the mechanism of background occurrence is the flushing of bacterial and viral detritus into swallow holes by surface run-off as was observed by Harold (1937) for bacterial species.

In addition to the limited knowledge of the mechanisms of background occurrence, there is also uncertainty regarding phage survival and sorption, particularly specific data relating to the Chalk aquifer. Analytical modelling of phage breakthroughs did not require incorporation of either sorption or inactivation to derive a good model fit to observed data. However, it is possible that both processes may have been masked by the calibration of mass transfer coefficients. The attenuation of bacteriophage by dual porosity diffusive exchange is suggested by the close match of the DP-1D analytical modelling to observations and the plausibility of is supported by the small size of the phage relative to the matrix pore throats.

Experimental investigation of these effects in the Chalk would be beneficial and would aid selection of appropriate analytical models and parameter evaluation in future tracer studies.

The apparent difference in attenuation between the borehole injection and swallow hole injection tracer tests could be explained by the different methods of tracer injection. Direct input to a conduit is unlikely to have occurred in the two borehole injections given the apparent Darcy velocities derived by Fitzpatrick (2010). The difference in attenuation could therefore be explained by much of the tracer being lost in the highly dispersive and attenuating double porosity fracture system with only a small proportion reaching the karst conduits from the borehole injection sites. However, this mechanism cannot explain the highly attenuating pathways identified by (Maurice et al., 2006; Maurice, 2008) from direct swallow hole injection. Visual inspection of the form of the Vale of St Albans karst through in quarry outcrops (if any) or through sub-surface optical surveys would be beneficial.

9.4 Modelling the Karstic Chalk aquifer

Transport in the karstic Chalk aquifer has been shown to be the result of complex interaction of rapid low attenuation pathways superimposed upon the diffusive dual porosity exchange of the fractures and matrix. The equivalent porous media approach modelling adopted in this study represents an abstract simplification of these complex processes, and clearly at a local scale the modelling is unable to replicate fully the range of transport behaviour. Despite this limitation,on a catchment scale the assumption of porous media is more appropriate given the coarse grid size relative to the likely dimensions of conduits and fractures, and as such the model is able to approximate the essential behaviour that is relevant to the transport of bromate.

The spatial distribution of model parameters was developed to be consistent with the inferred geometry of the karst system that arose from the conceptual model of the karst function. This was further refined by calibration of the transport model against the tracer test data . By this approach, and the manner in which the fractured and karstic aquifer is represented as a “smeared” equivalent porous media, the model effective porosity, hydraulic conductivity and mass transfer coefficient effectively all become fitting parameters and hence do not necessarily relate exactly to values derived from empirical data or field tests. In this sense the model is calibrated for the purpose of replicating the characteristics of of karst transport to the Lee Valley and so should not be applied for other purposes.

That an approximate representation of transport within the Hertfordshire Chalk karst can be achieved is significant, since EPM models have previously not been able to replicate the tortuous flow paths in karst. This was achievable in Hertfordshire probably because the inferred karst flow paths in do not cross cut the groundwater equipotential contours of the more diffuse fracture system as a result of the driving head provided by the North Mymms recharge mound. As the Chalk aquifer is only locally and mildly karstic compared to more traditional karst aquifers such as the Mendip limestone (Maurice, 2008), the smaller scale of conduit and solution enlargement also allow a porous media approach to be an adequate representation at the model scale. Were this not the case, modelling appropriate flow directions would have been a greater challenge and would likely not have been achievable in a MODFLOW representation.

The development of discrete representations of karst in groundwater flow and transport models through either finite element representation or the adaptation of a CFP-MODFLOW (Conduit Flow Processes) would improve the representation of local scale processes. However this but would require additional parameterisation of the fracture and conduit properties and geometry than can be presently derived from, or validated by available field data. An EPM model therefore represents the most parsimonious approach currently possible. The representation of dual porosity diffusion as a first order mass transfer process remains a further limitation of the EPM approach.

Compounding the limitations arising from representation of aquifer processes by the model are uncertainties associated with input data and the understanding of aquifer processes, specifically the bromate source term which was shown during model calibration to control the form and magnitude of simulated breakthroughs but also in the representation and knowledge of dual porosity through a first order mass transfer process.

Further aquifer investigation, particularly cored boreholes from which the extent of matrix contamination could be measured by pore water extraction would contribute significantly to estimates of the distribution of mass within the aquifer, which could then better constrain the likely source term. It would also allow better characterisation of the diffusive process.

The modelling has also helped to inform and refine the conceptual understanding of karst function with respect to contaminant transport, particularly within the Vale of St Albans. Travel times of the assumed 1983-1987 recharge pulse to receptors imply that the majority of this mass has moved at a similar rate the average Darcy velocity ($\approx$ 1m/day) identified by the single borehole dilution testing of Fitzpatrick (2010) and assumed to be representative of the non karstic fracture system. This has implied that karst, at least in the manner in which it was represented in the model, is not the dominant transport process in the Vale of St Albans.

9.5 Future of the Bromate Contamination

The overriding objective of the work presented in this thesis has been to improve the understanding of Chalk karst in Hertfordshire with respect to its influence upon the transport of bromate and to incorporate that understanding into predictions of the long term behaviour of bromate. The new conceptual understanding and modelling approaches presented have identified the following conditions of particular relevance to bromate contamination:

- Extensive contamination of the Chalk matrix is implied to have occurred in the Vale of St Albans and Hatfield.

- Whilst karst is present in the Vale of St Albans, it does not exert a significant influence upon bromate concentrations, which are dominated by matrix-fracture diffusive exchange. This implies that either the karst is highly attenuating, or limited in extent and connectivity to the main bromate bearing fractures. However, the karst may influence short term (day to day) variations in concentration imposed on the long term and seasonal trends.

- East of the Hatfield area, bromate transport becomes dominated by rapid, low attenuation karstic routes. Contribution of transport from the fracture and matrix system in this region is limited and may be localised around the main flow routes and conduits.

- Modelling suggests that the annual seasonal dilution observed at Essendon PWS, Arkley Hole and locations in the Lee Valley can be accounted for by allogenic recharge to the karst system, particularly from Water End

- The effect of Hatfield PWS when acting as a scavenge pumping well is to exert a direct influence upon the karst flow system; despite this the possible $\Phi X174$ tracer bypass of Hatfield PWS, and the observation that even under scavenging conditions potentially harmful concentrations are observed in the Lee Valley, imply that the scavenging effect is somewhat limited.

- Modelling indicates that the majority of bromate mass has left the St Leonard's court site and migrated into the Vale of St Albans, if this is the case the effectiveness of a scavenge pumping well developed at a near-source location may be limited. To validate this, the bromate source fluxes and distribution of mass within the aquifer should be subject to further field investigation.

Considered in combination, these results suggest that major challenges still remain in understanding, predicting and managing the impact of bromate. Modelled and observational evidence of the distribution of bromate suggests that extensive contamination of the Chalk matrix has occurred in the Vale of St Albans. Although uncertainty associated with the modelling prohibits a precise estimate of the likely duration and magnitude of contamination, it is clear from the modelled predictions and empirical estimates of Chalk diffusion times (e.g Barker et al., 2000; Watson, 2004; Fretwell, 1999) that the contamination is likely to persist at hazardous levels for at least several decades. Source terms as defined by Fitzpatrick (2010) suggest release of bromate will continue from St Leonard's Court Model until at least 2100 and given the slow average travel time through the vale of St Albans (model estimates suggest $\approx$ 20 years) and back diffusion from the matrix (which is not accounted for in the MT3D representation of dual porosity) will further prolong the duration of contamination.

The long-term evolution of bromate concentrations at the Lee Valley is complicated by the influence of the karst system. At present it appears that the majority of bromate mass reaching the Lee Valley travels via rapid, low attenuation karstic routes, with only limited contribution from the fracture and matrix systems. Scavenge abstraction from Hatfield PWS is able to reduce these concentrations. Given that these locations have shown connections to karstic flows, and given the close agreement of response times, the scavenging influence of Hatfield PWS upon the karst system is likely to be effective.

Although the absolute magnitude of the scavenging effect in the Lee Valley is limited, the magnitude of response needs to be evaluated against the likely effectiveness of any new scavenge pumping location, particularly considering that extensive contamination of Chalk pore water in the Vale of St Albans has probably occurred. In order to exert a similar, or more efficient, influence than the Hatfield PWS, a scavenge pumping location would need to be able to draw upon a significant volume of contaminated aquifer (i.e. be in a well fractured and connected part of the aquifer) and would need to also need to exert a strong influence upon the karst system. Hatfield PWS is already well positioned since it is on the margins of the main karst zone and has been proven to be connected to the karst input at Water End either by construction or by development of the aquifer around the borehole during its pumping history. Given the limited scale of karst development in the Chalk, establishing an equally effective connection within the Vale of St Albans is likely to be more challenging, especially as the nature of the relationship between the Vale of St Albans and near Palaeocene feather edge karst is more uncertain. It is unlikely that disruption of just one or two conduits, as may be encountered in an ideal borehole, will result in a significant improvement at downgradient locations.

Development of any scavenge pumping borehole will require investigations of upgradient and downgradient connectivity under both pumping and non-pumping conditions in order to be able to establish with confidence whether it will be effective as a remediation method in the long term. Scavenge pumping in combination with Hatfield PWS and/or other boreholes might be necessary in order to provide robust protection, especially since active flow directions and karst conduits are inferred to vary with changing water levels and the imposed aquifer stress.

Bromate is likely to remain a water quality problem in Hertfordshire for the foreseeable future. The work presented in this thesis has developed and improved our understanding of the aquifer and in particular the function of the Chalk karst. However, the ability to make accurate long term predictions of bromate behaviour remains significantly impaired by lack of knowledge relating to the present spatial distribution of bromate (i.e. how much mass resides in the aquifer matrix and where does it occur) and in the temporal description of the source term. Until these can be quantified with some confidence the true deficiencies in the modelling approaches cannot be properly addressed. The analytical modelling of Fitzpatrick (2010), which is based in part upon the conceptual understanding and modelling approach developed in this thesis, will be able to make predictions of porewater bromate concentrations along principal flowpaths. However, these predictions cannot be validated against any field observations at the current time.

It is an essential requirement that one, or several, cored investigatory boreholes are drilled, distributed across the affected aquifer and the apparent bromate “plume” within the Vale of St Albans in order to establish without doubt the extent of bromate contamination of Chalk pore water and the site-specific properties of the fracture and karst system. Only on this basis could a robust estimate of the long term impact of bromate contamination be further evaluated and an effective strategy for aquifer remediation be determined.

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Appendix A

Swallow Hole Mapping of Hatfield Park

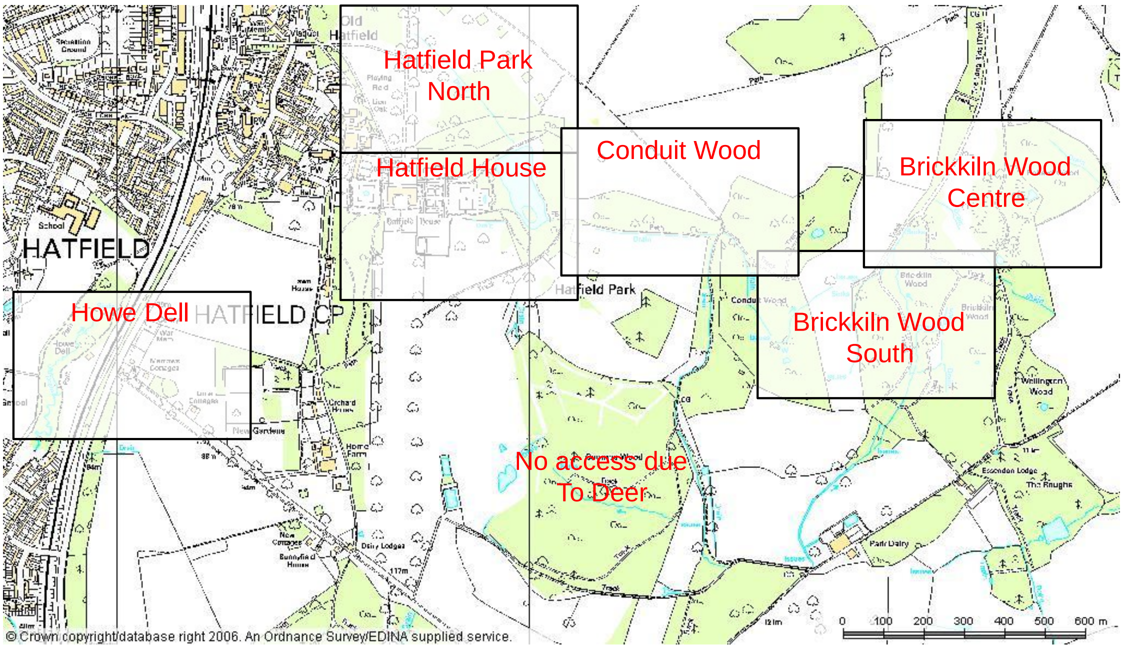


Figure A.1: Hatfield Park North

Figure A.2: Howe Dell Swallow Holes

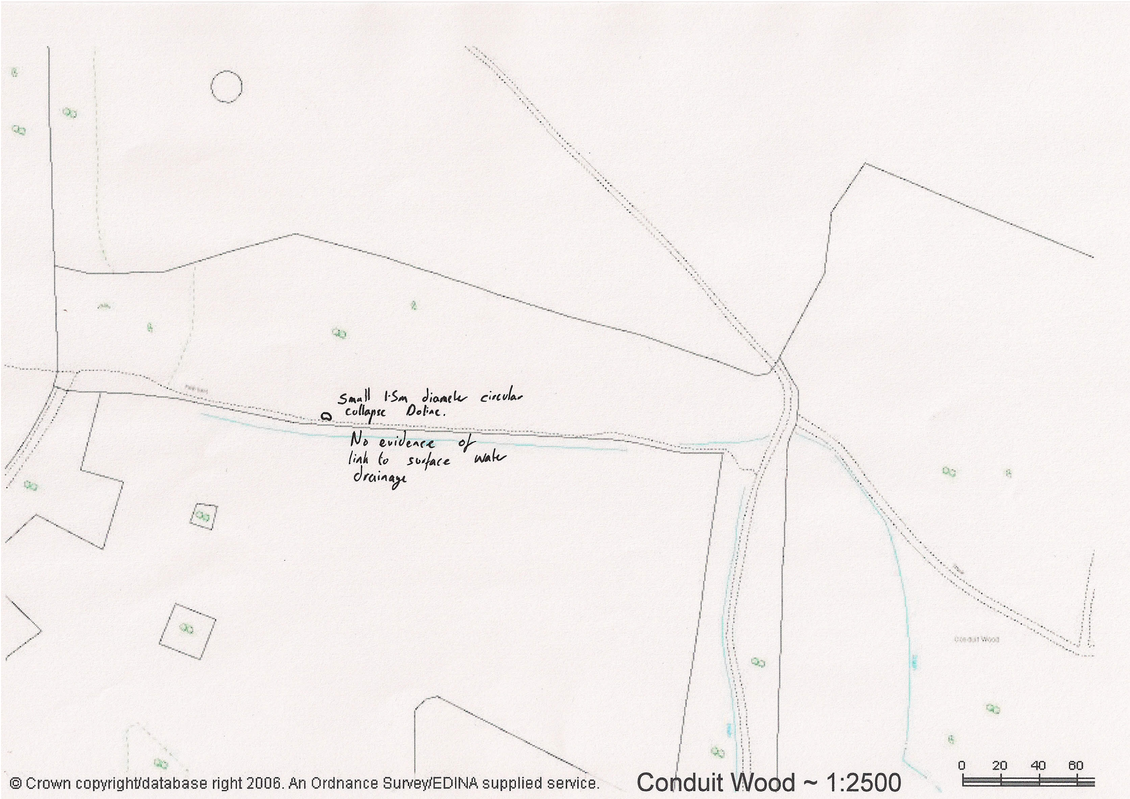


Figure A.3: Conduit Wood

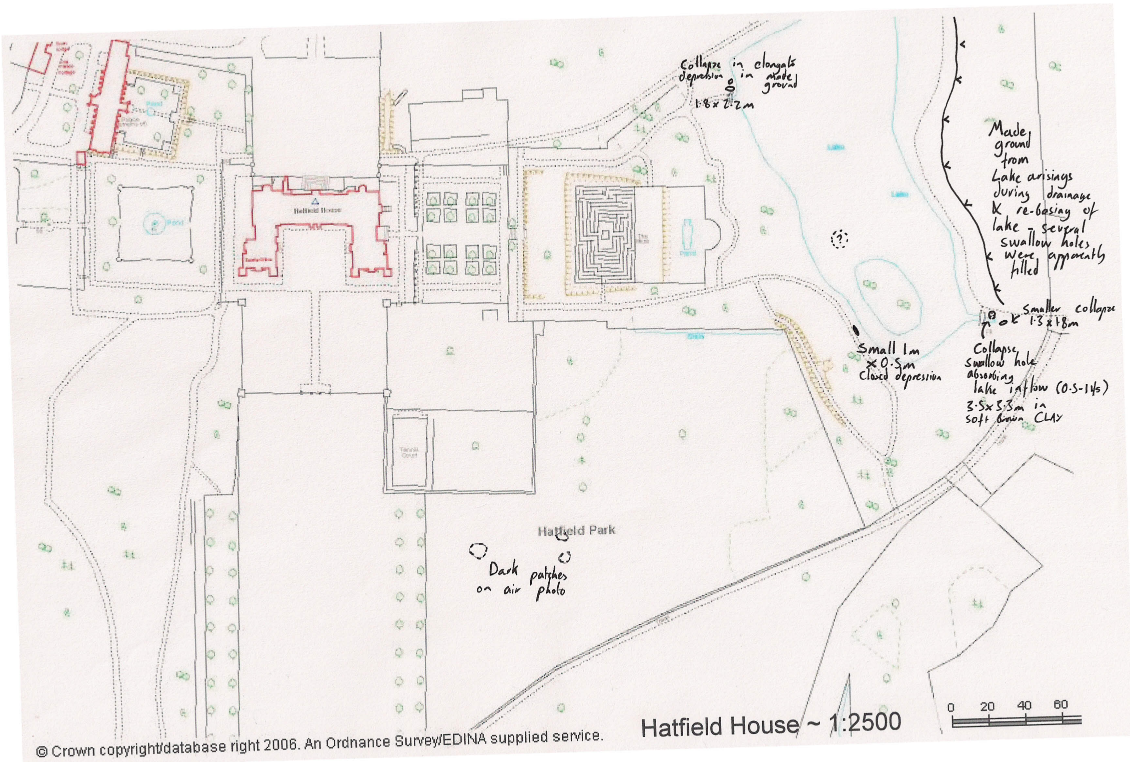


Figure A.4: Hatfield House

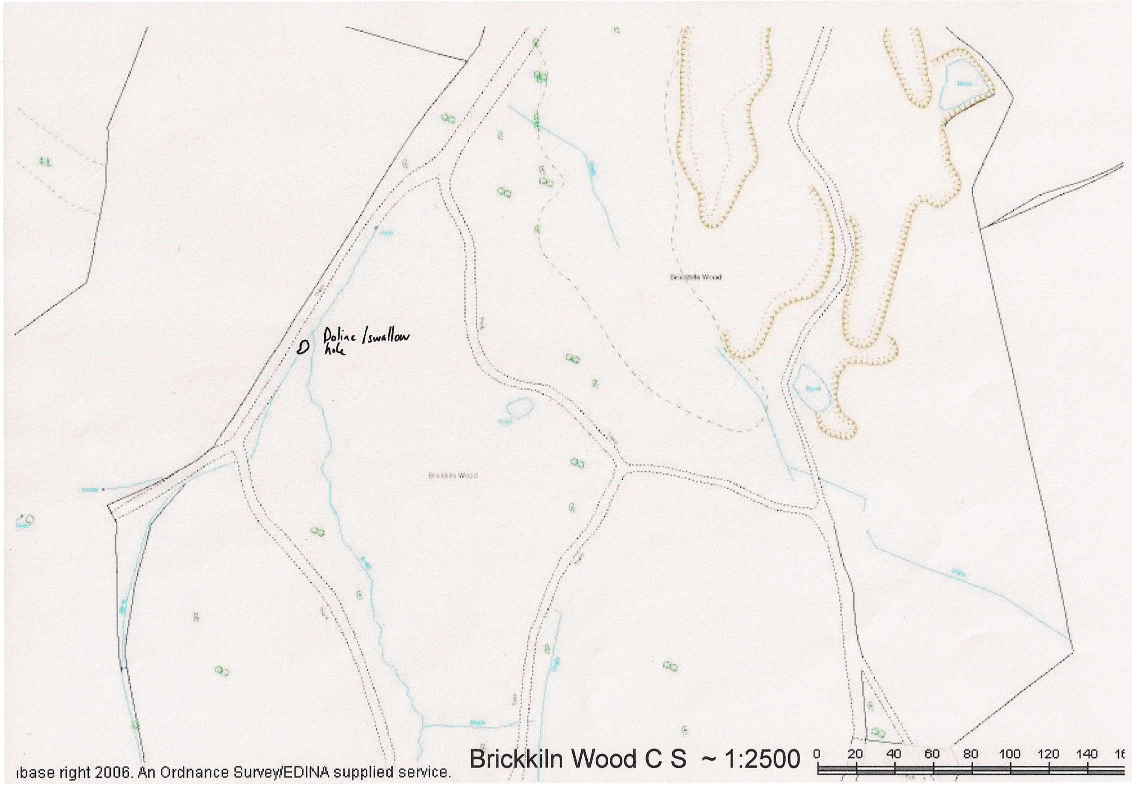


Figure A.5: Brickkiln Wood South

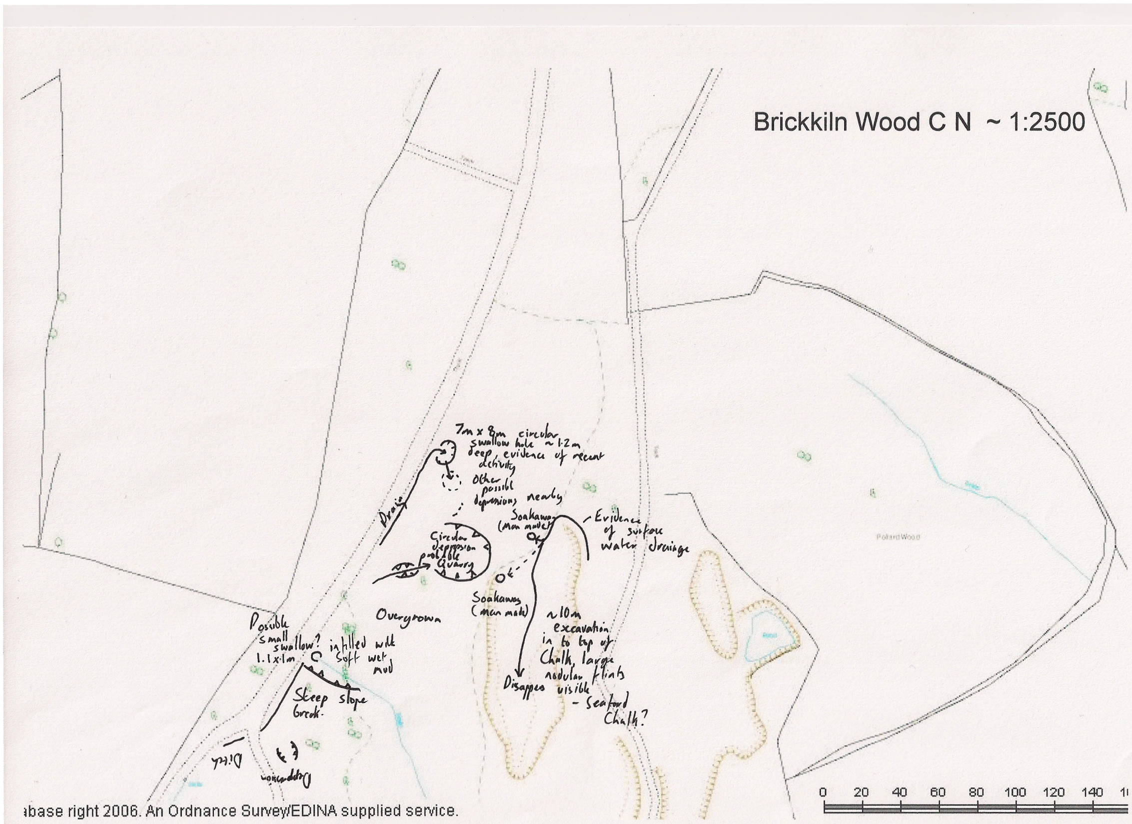


Figure A.6: Brickkiln Wood Central

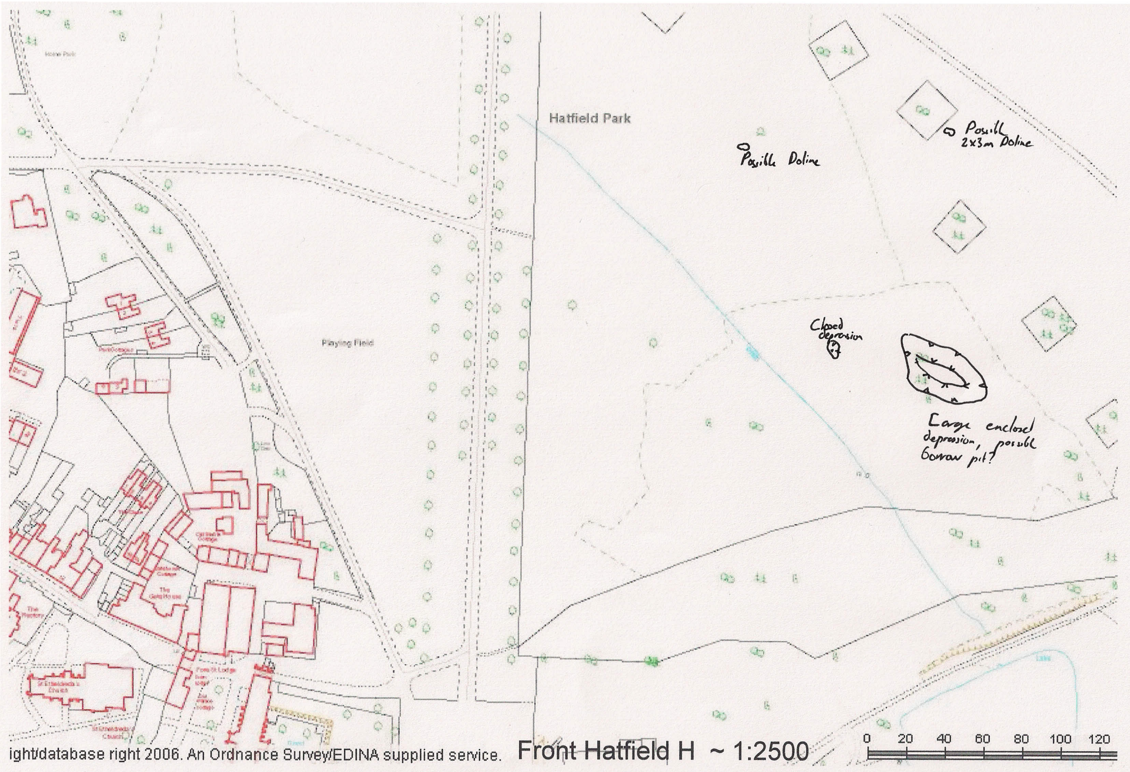


Figure A.7: Hatfield Park North

Appendix B

Development of the Tracer Test Strategy

As discussed in Chapter 5 development of an overall strategy for the tracer testing was an interative processes that underwent a number of revisions during development relating to technical, resource or timing constraints.

Table B.1 summarises the development of the tracer proposal actually implemented. It indicates the objectives and scope of the initial proposals, injection and sampling locations and reasons for rejection and revision.

The methodology of the implemented tracer test was largely developed from the anciallary proposals, 2b and 2c. The injection of tracer at Comet way was initially put forward in proposal 2, and was adopted into the final proposal as a proxy for Hatfield PWS and to provide information on the westward extent of karst flows in the Hatfield area.

Table B.1: History of tracer proposals put forward by the author to be considered by VWTV, TWUL and the Environment Agency

Proposal	Objectives	Injection locations	Sampling locations	Tracer	Reason rejected
1	1) Establish connectivity between Hatfield PWS, Essendon PWS, local karst features and the Lee Valley. If possible, investigate connectivity variation under different pumping and seasonal conditions. 2) Once connections are established retrace using a conservative tracer to determine quantitative breakthrough curves	Hatfield PWS, Essendon PWS, Hatfield Park swallow holes, Water End swallow holes	Essendon PWS, Hatfield PWS, Lee Valley wells	Initially, Bacteriophage. For the conservative tracer; Flourescein or photine	Scope too ambitious and complex, Abstraction variations at Hatfield PWS limited by the resulting impact on downgradient water quality. Concern over water quality impacts of a dye/optical
2	Investigate the role of scavenge pumping at Hatfield PWS and establish extent and influence upon karst flows in the Hatfield area.	Comet Way OBH, Park Street OBH, Hatfield Park swallow holes	Hatfield PWS, Essendon PWS, Arkley Hole Spring, Chadwell Spring, Lynchmill Spring, observation wells in the area between Hatfield and Essendon	Bacteriophage	Concern about activity and connection of Hatfield Park swallow holes, Sampling regieme too onerous, cost too high. Abstraction variations at Hatfield PWS limited by the resulting impact on downgradient water quality.
2a	Ancilliary proposal to 2, inject tracer at or nearby Hatfield PWS when abstraction suspended to trace movement under natural gradient conditions to downgradient locations	Hatfield PWS	Essendon PWS, Arkley Hole, Chadwell Spring, Lynchmill Spring and Lee Valley wells	Bacteriophage	Abstraction suspension at Hatfield PWS prevent by the resulting impact on downgradient water quality.
2b	Ancilliary proposal to 2, inject tracer at Sandridge near bromate source to tracer bromate movement and transport properties	Observation borehole in the Sandridge area	As adopted tracer proposal	Bacteriophage	-
2c	Ancilliary proposal to 2, inject tracer at the Water End swallow hole complex to quantitatively repeat the experiments of Harold (1937) and establish if a connection to Hatfield PWS and Essendon PWS exists	Water End swallow holes	As adopted proposal	Bacteriophage	-

Appendix C

Raw Data from the Catchment Scale Tracer Tests

(a) Hatfield PWS

Time (HH:MM)	Date (DD/MM/YYYY)	Bacteriophage $MS2$ (pfu/ml)	Bacteriophage $\Phi X174$ (pfu/ml)	Bacteriophage *Serratia Marcescens* (pfu/ml)	Abstraction (Ml/day)
11:03	04/03/2008	0	0	0	5.99
09:25	05/03/2008	0	0	230	5.99
11:30	06/03/2008	0	0	12	6.00
14:15	07/03/2008	0	0	1	5.95
11:19	08/03/2008	0	0	0	6.00
10:47	09/03/2008	0	0	1	6.00
15:20	10/03/2008	0	0	0	5.99
11:55	11/03/2008	1	0	0	6.00
12:38	12/03/2008	0	1	0	5.99
13:00	13/03/2008	0	0	0	5.99
12:45	14/03/2008	0	0	0	5.99
10:39	15/03/2008	0	0	0	5.99
10:40	16/03/2008	0	0	0	5.99
09:47	18/03/2008	1	1	0	6.00
11:50	20/03/2008	0	0	-	5.99
08:51	25/03/2008	0	0	-	5.87
12:50	27/03/2008	-	0	0	5.89
09:02	31/03/2008	0	0	-	5.99
10:50	01/04/2008	0	0	-	6.00
10:50	02/04/2008	0	0	-	6.00
11:50	03/04/2008	0	0	-	5.99
08:35	03/04/2008	0	0	0	5.99
12:15	04/04/2008	0	0	-	5.99
09:36	05/04/2008	0	2	-	5.99
10:11	06/04/2008	0	0	-	5.99
13:04	07/04/2008	0	0	-	5.99
10:00	08/04/2008	0	0	-	2.60
11:25	09/04/2008	0	0	-	3.99
10:02	10/04/2008	0	0	-	6.00
12:05	10/04/2008	0	0	-	6.00
10:45	11/04/2008	0	0	-	6.00
10:10	12/04/2008	0	0	-	6.00
10:42	13/04/2008	0	0	-	5.99
13:28	14/04/2008	0	0	-	6.00
10:42	15/04/2008	0	0	-	6.00
11:57	16/04/2008	0	0	-	5.99
10:55	17/04/2008	0	0	-	5.99
09:23	18/04/2008	0	0	-	5.99
11:05	18/04/2008	0	0	-	5.99

(b) Essendon PWS

Time (HH:MM)	Date (DD/MM/YYYY)	Bacteriophage $MS2$ (pfu/ml)	Bacteriophage $\Phi X174$ (pfu/ml)	Bacteriophage *Serratia Marcescens* (pfu/ml)	Abstraction (Ml/day)
10:46	04/03/2008	0	0	0	5.19
08:30	05/03/2008	1	0	0	5.23
11:05	06/03/2008	0	0	766	5.61
13:50	07/03/2008	0	0	18	5.48
11:03	08/03/2008	0	0	6	5.79
10:06	09/03/2008	0	0	39	5.17
15:04	10/03/2008	0	1	8	2.938
11:41	11/03/2008	0	6	7	2.75
11:06	12/03/2008	0	0	6	3.23
10:20	14/03/2008	1	0	6	3.83
09:50	15/03/2008	2	0	5	3.83
09:46	16/03/2008	0	0	0	3.82
08:36	18/03/2008	0	0	3	3.26
11:35	20/03/2008	1	0	0	2.49
08:06	25/03/2008	1	2	0	3.08
12:25	27/03/2008	-	0	0	2.82
08:41	31/03/2008	2	2	-	4.13
10:30	01/04/2008	1	1	-	4.32
08:16	03/04/2008	0	0	-	3.86
11:30	03/04/2008	0	1	-	3.86
11:55	04/04/2008	0	0	-	4.07
09:22	05/04/2008	0	0	-	4.82
09:56	06/04/2008	0	0	-	3.27
09:18	08/04/2008	0	0	-	5.41
11:05	09/04/2008	1	0	-	5.33
09:41	10/04/2008	0	1	-	4.54
11:45	10/04/2008	0	0	-	4.54
10:25	11/04/2008	0	0	-	5.88
09:48	12/04/2008	-	-	-	5.91
10:18	13/04/2008	0	0	-	5.91
12:52	14/04/2008	0	0	-	5.91
10:21	15/04/2008	0	0	-	5.91
10:30	16/04/2008	0	1	-	5.04
08:50	18/04/2008	1	-	-	5.86
10:45	18/04/2008	0	0	-	5.86

(c) Coleman Green Lane

Time (HH:MM)	Date (DD/MM/YYYY)	$MS2$ Coliphage (pfu/ml)	Water Level (mbgl)
12:15	04/03/2008	0	3.82
09:17	06/03/2008	0	3.7
14:16	10/03/2008	0	3.71
10:55	12/03/2008	0	3.76
11:15	14/03/2008	0	3.79
13:07	17/03/2008	1	3.74
13:45	10/04/2008	0	3.54
16:30	23/04/2008	0	3.56

(d) Nashes Farm

Time (HH:MM)	Date (DD/MM/YYYY)	$MS2$ Coliphage (pfu/ml)	Water level (mOD)
12:44	04/03/2008	1	74.94
09:52	06/03/2008	0	74.95
12:13	10/03/2008	0	75.03
12:25	11/03/2008	0	75.03
11:58	14/03/2008	0	74.98
13:32	17/03/2008	0	75.04
13:50	01/04/2008	0	75.17
13:10	03/04/2008	0	75.15
14:37	08/04/2008	0	75.23
13:30	10/04/2008	0	75.24
14:10	16/04/2008	0	75.18
15:45	23/04/2008	0	75.18
10:46	30/04/2008	0	75.23

(e) Capps Cottage

Time (HH:MM)	Date (DD/MM/YYYY)	$MS2$ Coliphage (pfu/ml)	Water level (mOD)
11:25	04/03/2008	0	74.86
10:06	06/03/2008	0	74.85
10:00	09/03/2008	0	74.86
12:02	10/03/2008	1	74.96
12:10	11/03/2008	0	74.93
11:36	14/03/2008	0	74.86
13:45	17/03/2008	0	74.90
13:34	01/04/2008	0	75.03
13:20	03/04/2008	0	75.04
13:15	10/04/2008	0	75.12
14:25	18/04/2008	0	75.12
16:05	23/04/2008	0	75.08
10:36	30/04/2008	0	-

(f) Fairfolds Farm

Time (HH:MM)	Date (DD/MM/YYYY)	$MS2$ Coliphage (pfu/ml)	Water Level (mOD)
11:35	04/03/2008	0	-
10:16	06/03/2008	0	73.90
11:49	10/03/2008	1	74.00
11:55	11/03/2008	0	73.97
11:38	14/03/2008	0	73.92
13:52	17/03/2008	0	74.89
13:21	01/04/2008	0	74.06
13:35	03/04/2008	0	74.05
13:05	10/04/2008	0	74.14
14:10	18/04/2008	0	77.15
16:15	23/04/2008	0	74.01
10:30	30/04/2008	0	73.17

(g) Hatfield Quarry WM13

Time (HH:MM)	Date (DD/MM/YYYY)	$MS2$ Coliphage (pfu/ml)	Water Level (mOD)
14:10	04/03/2008	-	73.68
11:24	06/03/2008	0	73.67
13:16	10/03/2008	0	73.82
12:02	12/03/2008	0	72.63
12:30	14/03/2008	0	72.67
15:01	17/03/2008	0	73.78
14:10	03/04/2008	1	73.90
13:20	08/04/2008	0	73.96
12:45	14/04/2008	0	73.93
14:35	23/04/2008	0	73.94
09:50	30/04/2008	0	73.93

(h) Hatfield Quarry WM12

Time (HH:MM)	Date (DD/MM/YYYY)	$MS2$ Coliphage (pfu/ml)	Water Level (mOD)
13:50	04/03/2008	-	72.52
11:02	06/03/2008	0	72.60
12:59	10/03/2008	0	72.79
11:43	12/03/2008	0	73.11
12:48	14/03/2008	0	72.58
14:44	17/03/2008	0	72.62
14:50	03/04/2008	8	73.83
14:15	08/04/2008	1	73.02
13:45	14/04/2008	0	72.97
15:25	23/04/2008	0	72.98
10:20	30/04/2008	0	73.00

(i) Hatfield Quarry WM8

Time (HH:MM)	Date (DD/MM/YYYY)	$MS2$ Coliphage (pfu/ml)	Water Level (mOD)
13:26	04/03/2008	2	71.34
10:42	06/03/2008	0	71.39
12:42	10/03/2008	0	71.61
11:29	12/03/2008	0	71.40
13:01	14/03/2008	0	71.38
14:31	17/03/2008	0	71.44
14:35	03/04/2008	0	70.69
13:55	08/04/2008	0	71.67
13:15	14/04/2008	0	71.63
15:05	23/04/2008	0	71.63
10:05	30/04/2008	0	71.68

(j) Hatfield Business Park

Time (HH:MM)	Date (DD/MM/YYYY)	$MS2$ Coliphage (pfu/ml)	Water Level (mOD)
10:49	07/03/2008	0	64.23
12:40	12/03/2008	0	64.11
13:34	14/03/2008	0	64.10
12:20	18/03/2008	0	64.09

(k) North Mymms PWS

Time (HH:MM)	Date (DD/MM/YYYY)	*Serratia Marcescens* Phage (pfu/ml)
13:25	07/03/2008	0
10:21	08/03/2008	0
10:32	09/03/2008	0
14:33	10/03/2008	0
11:24	11/03/2008	0
12:19	12/03/2008	1
12:42	13/03/2008	0
10:00	14/03/2008	0
10:28	15/03/2008	0
10:18	16/03/2008	0
09:10	18/03/2008	0
11:14	20/03/2008	0
08:36	25/03/2008	0

(l) Park Street OBH

		Bacteriophage			
Time (HH:MM)	Date (DD/MM/YYYY)	$MS2$ (pfu/ml)	$\Phi X174$ (pfu/ml)	*Serratia Marcescens* (pfu/ml)	Water Level (mOD)
11:25	07/03/2008	-	0	0	51.16
12:34	09/03/2008	-	0	0	50.96
12:20	12/03/2008	-	0	0	50.85
13:45	15/03/2008	-	0	0	51.18
13:17	18/03/2008	-	0	0	
12:15	03/04/2008	0	0	-	51.72
15:55	10/04/2008	0	0	-	51.18
13:40	18/04/2008	0	0	-	51.55
17:15	23/04/2008	0	0	-	51.17

(m) Arkley Hole Spring

Time (HH:MM)	Date (DD/MM/YYYY)	Bacteriophage $MS2$ (pfu/ml)	$\Phi X174$ (pfu/ml)	*Serratia Marcescens* (pfu/ml)	Notes
09:16	04/03/2008	1	0	0	-
22:11	04/03/2008	-	-	0	-
10:11	05/03/2008	0	0	0	-
18:33	05/03/2008	0	0	0	-
02:33	06/03/2008	-	0	225	-
10:33	06/03/2008	0	0	3360	-
18:33	06/03/2008	-	0	382	-
02:33	07/03/2008	-	1	87	-
10:33	07/03/2008	0	1	42	-
18:33	07/03/2008	-	-	21	-
02:33	08/03/2008	-	-	14	-
10:33	08/03/2008	0	0	12	-
18:33	08/03/2008	-	-	10	-
02:33	09/03/2008	-	-	3	-
10:33	09/03/2008	0	0	9	-
18:33	09/03/2008	-	-	16	-
02:33	10/03/2008	0	0	8	-
23:10	10/03/2008	-	-	3	-
11:10	11/03/2008	0	0	62	-
23:10	11/03/2008	-	-	5	-
11:17	12/03/2008	0	3	6	-
11:17	13/03/2008	0	1	0	-
11:25	14/03/2008	0	1	0	-
23:25	14/03/2008	-	- 1	-	
11:25	15/03/2008	0	0	0	-
23:25	15/03/2008	-	-	1	-
11:25	16/03/2008	1	0	0	-
23:25	16/03/2008	-	-	0	-
11:25	17/03/2008	3	2	0	High turbidty in samples
23:25	17/03/2008	-	-	1	High turbidty in samples
11:47	18/03/2008	-	1	1	Spring flow higher than previously seen and high turbidity
23:47	18/03/2008	0	0	-	-
11:47	19/03/2008	-	0	0	-
23:47	19/03/2008	1	0	-	-
11:47	20/03/2008	-	0	0	Turbidity has dropped, flow still vigorous
01:30	21/03/2008	0	0	-	-
13:30	21/03/2008	-	1	0	-
01:30	22/03/2008	0	0	-	-
13:30	22/03/2008	-	0	0	-
01:30	23/03/2008	0	-	-	-
13:30	23/03/2008	-	0	0	-
01:30	24/03/2008	0	-	-	-
13:30	24/03/2008	-	0	0	-
01:30	25/03/2008	0	-	-	-
12:42	25/03/2008	-	0	0	-
12:57	26/03/2008	2	0	-	-
12:57	27/03/2008	1	1	-	-
12:57	28/03/2008	0	0	-	-
12:57	29/03/2008	0	0	-	-
12:57	30/03/2008	0	0	-	-
12:57	31/03/2008	0	0	-	-
10:45	01/04/2008	0	0	-	High flow, estimated $\approx$ 0.3m^3/s, some turbidity
10:00	02/04/2008	0	1	-	-
09:37	03/04/2008	0	0	-	Moderate flow, estimated $\approx$ 0.078m^3/s, clearer water than previously
08:47	04/04/2008	0	0	-	
08:47	05/04/2008	0	0	-	
08:47	06/04/2008	0	0	-	
08:47	07/04/2008	0	0	-	
08:47	08/04/2008	0	0	-	
20:47	08/04/2008	0	0	-	
08:47	09/04/2008	0	0	-	
20:47	09/04/2008	1	0	-	
08:47	10/04/2008	0	0	-	Moderate flow, estimated $\approx$ 0.084m^3/s, very clear water
09:09	11/04/2008	0	0	-	
09:09	12/04/2008	0	0	-	
09:09	13/04/2008	0	0	-	
09:09	14/04/2008	0	0	-	Moderate flow, estimated $\approx$ 0.069m^3/s, very clear water
11:43	16/04/2008	0	0	-	
10:43	17/04/2008	0	0	-	
10:43	18/04/2008	0	0	-	Moderate flow, estimated $\approx$ 0.11m^3/s, very clear water
12:07	19/04/2008	0	0	-	
12:07	20/04/2008	0	0	-	
12:07	21/04/2008	0	0	-	
12:07	22/04/2008	0	0	-	
12:07	23/04/2008	0	0	-	Moderate flow, estimated $\approx$ 0.078m^3/s, very clear water
12:24	24/04/2008	0	0	-	
12:24	25/04/2008	0	0	-	
12:24	26/04/2008	0	0	-	
12:24	27/04/2008	0	1	-	
12:24	28/04/2008	0	0	-	
12:24	29/04/2008	1	0	-	

(n) Chadwell Spring

		Bacteriophage			
Time (HH:MM)	Date (DD/MM/YYYY)	$MS2$ (pfu/ml)	$\Phi X174$ (pfu/ml)	*Serratia Marcescens* (pfu/ml)	Notes
10:27	04/03/2008	0	0	0	
11:17	05/03/2008	0	0	0	Small trickle over weir $< 0.0001\text{m}^3/\text{s}$
12:50	06/03/2008	0	0	0	No flow over weir
09:59	07/03/2008	0	0	0	Small trickle over weir $< 0.0001\text{m}^3/\text{s}$
10:03	08/03/2008	-	0	0	Small trickle over weir $< 0.0001\text{m}^3/\text{s}$
11:40	09/03/2008	0	0	0	Flow slightly increased
09:12	10/03/2008	-	0	0	Vigorous flow over small weir and slightly overtopping main weir in strong wind
11:34	11/03/2008	0	0	0	Highest flow observed, overtopping small and main weir
11:10	13/03/2008	0	0	0	Moderate flow, higher turbidity than previously
12:30	15/03/2008	0	0	0	
11:32	18/03/2008	1	0	0	Moderate flow $\approx 0.050 - 0.1\text{m}^3/\text{s}$, water cloudy and turbid
11:40	03/04/2008	1	0	0	Moderate flow $\approx 0.01 - 0.015\text{m}^3/\text{s}$, water clear
15:40	08/04/2008	1	0	-	
15:20	10/04/2008	0	1	-	
13:15	16/04/2008	0	0	-	Flow reduced $\approx 0.005 - 0.01\text{m}^3/\text{s}$, water clear
12:15	18/04/2008	0	0	-	
12:30	23/04/2008	0	0	-	Flow $\approx 0.005 - 0.01\text{m}^3/\text{s}$, water very clear
11:35	30/04/2008	0	0	-	

(o) Turnford PWS

		Bacteriophage		
Time (HH:MM)	Date (DD/MM/YYYY)	$MS2$ (pfu/ml)	$\Phi X174$ (pfu/ml)	*Serratia Marcescens* (pfu/ml)
09:00	06/03/2008	-	-	0
12:00	07/03/2008	-	-	0
12:00	10/03/2008	-	-	262
08:54	12/03/2008	-	-	51
10:35	17/03/2008	-	-	36
08:40	19/03/2008	-	2	6
08:55	25/03/2008	-	0	3
08:45	03/04/2008	0	0	0
16:26	04/04/2008	1	1	-
11:40	07/04/2008	0	0	-
13:15	08/04/2008	0	0	-
10:45	09/04/2008	0	0	-
10:59	10/04/2008	0	2	-
Unknown	11/04/2008	0	0	-
14:04	14/04/2008	0	0	-
12:00	15/04/2008	0	1	-
08:40	16/04/2008	0	0	-
10:30	17/04/2008	0	0	-
13:30	18/04/2008	0	0	-
11:00	21/04/2008	0	0	-
09:46	23/04/2008	0	0	-

(p) New River at Kings Mead

Time (HH:MM)	Date (DD/MM/YYYY)	Bacteriophage $MS2$ (pfu/ml)	$\Phi X174$ (pfu/ml)	*Serratia Marcescens* (pfu/ml)
11:30	03/04/2008	0	2	-
15:30	08/04/2008	0	2	-
15:15	10/04/2008	0	0	-
13:10	16/04/2008	0	1	-
12:10	18/04/2008	0	0	-
12:25	23/04/2008	1	5	-
11:30	30/04/2008	0	0	-

(q) New River at Emma's Well

Time (HH:MM)	Date (DD/MM/YYYY)	Bacteriophage $MS2$ (pfu/ml)	$\Phi X174$ (pfu/ml)	*Serratia Marcescens* (pfu/ml)
11:08	03/04/2008	0	4	-
11:32	08/04/2008	1	0	-
14:55	10/04/2008	0	4	-
11:30	14/04/2008	0	0	-
12:50	16/04/2008	2	0	-
11:55	18/04/2008	0	0	-
12:10	23/04/2008	1	1	-

(r) New River at Amwell Marsh

Time (HH:MM)	Date (DD/MM/YYYY)	Bacteriophage $MS2$ (pfu/ml)	$\Phi X174$ (pfu/ml)	*Serratia Marcescens* (pfu/ml)
09:18	08/03/2008	-	0	22
11:20	09/03/2008	0	2	16
10:55	11/03/2008	8	4	2
09:31	14/03/2008	0	1	0
11:54	15/03/2008	0	3	0
11:07	18/03/2008	2	3	0
12:29	20/03/2008	0	1	0
12:40	01/04/2008	0	3	0
11:10	03/04/2008	2	3	0
11:35	08/04/2008	0	1	-

(s) Amwell Marsh PWS

Time (HH:MM)	Date (DD/MM/YYYY)	Bacteriophage $MS2$ (pfu/ml)	$\Phi X174$ (pfu/ml)	*Serratia Marcescens* (pfu/ml)
09:25	06/03/2008	0	0	0
12:20	07/03/2008	0	0	0
12:20	10/03/2008	0	0	23
09:56	12/03/2008	0	0	6
11:05	17/03/2008	1	1	0
09:15	19/03/2008		2	0
10:12	25/03/2008		1	0
09:30	03/04/2008	0	0	0
16:45	04/04/2008	0	0	-
12:15	07/04/2008	0	0	-
13:30	08/04/2008	0	3	-
10:59	09/04/2008	2	3	-
11:05	10/04/2008	0	0	-
Unknown	11/04/2008	0	0	-
12:45	14/04/2008	0	0	-
13:10	15/04/2008	0	0	-
09:00	16/04/2008	0	0	-
10:45	17/04/2008	0	0	-
13:46	18/04/2008	0	0	-
11:20	21/04/2008	0	0	-
10:44	23/04/2008	0	0	-
14:50	23/04/2008	0	0	-

(t) Rye Common PWS

Time (HH:MM)	Date (DD/MM/YYYY)	Bacteriophage $MS2$ (pfu/ml)	$\Phi X174$ (pfu/ml)	*Serratia Marcescens* (pfu/ml)
09:40	06/03/2008	-	-	0
12:15	07/03/2008	-	-	0
12:15	10/03/2008	-	0	1
09:46	12/03/2008	-	0	3
10:50	17/03/2008	-	-	1
09:00	19/03/2008	-	0	0

(u) Lynchmill Spring

Time (HH:MM)	Date (DD/MM/YYYY)	Bacteriophage $MS2$ (pfu/ml)	$\Phi X174$ (pfu/ml)	*Serratia Marcescens* (pfu/ml)	Notes
19:50	05/03/2008	-	-	0	
03:50	06/03/2008	-	-	0	
11:50	06/03/2008	0	0	0	
19:54	06/03/2008	-	-	0	
03:54	07/03/2008	-	-	0	
11:54	07/03/2008	0	0	53	
19:54	07/03/2008	-	-	1200	
03:54	08/03/2008	-	-	1224	
08:56	08/03/2008	-	-	492	
12:56	08/03/2008	-	-	496	
16:56	08/03/2008	-	-	438	
20:56	08/03/2008	-	-	180	
00:56	09/03/2008	-	-	94	
04:56	09/03/2008	-	-	84	
08:56	09/03/2008	1	0	59	Discharge increased
19:03	09/03/2008	-	-	36	
07:03	10/03/2008	0	2	32	
19:03	10/03/2008	-	-	21	
07:03	11/03/2008	0	0	31	
21:58	11/03/2008	-	-	18	
09:58	12/03/2008	0	1	11	
04:53	13/03/2008	0	3	13	Discharge and turbidity has increased
11:21	15/03/2008	1	4	4	
23:32	15/03/2008	-	-	7	
11:32	16/03/2008	0	1	3	
23:32	16/03/2008	-	-	1	
11:32	17/03/2008	0	0	0	
23:32	17/03/2008	-	-	3	
22:46	18/03/2008	-	0	1	Greatest flow observed, $\approx 0.02-0.03\text{m}^3/\text{s}$ and turbid
10:46	19/03/2008	-	0	3	
22:46	19/03/2008	0	-	-	
10:46	20/03/2008	-	0	0	Flow $\approx 0.02 - 0.03\text{m}^3/\text{s}$ and turbid
10:57	21/03/2008	-	2	0	
22:57	21/03/2008	0	-	-	
10:57	22/03/2008	-	3	0	
10:57	23/03/2008	-	0	0	
22:57	23/03/2008	0	-	-	
10:57	24/03/2008	-	0	0	
10:57	25/03/2008	0	2	1	
22:57	25/03/2008	0	-	-	
10:57	26/03/2008	1	0	0	
10:57	27/03/2008	0	0	0	Flow $\approx 0.01 - 0.02\text{m}^3/\text{s}$ and clearer
12:31	28/03/2008	0	1	0	
00:31	29/03/2008	0	2	-	
12:31	29/03/2008	0	1	-	
12:31	30/03/2008	0	0	0	
12:31	31/03/2008	0	1	-	
12:00	01/04/2008	0	2	2	
11:16	02/04/2008	1	0	-	
10:43	03/04/2008	1	0	-	
09:52	04/04/2008	0	0	-	
09:52	05/04/2008	1	1	-	
09:52	06/04/2008	0	0	-	
09:52	07/04/2008	0	0	-	
21:52	07/04/2008	0	-	-	
09:52	08/04/2008	4	4	-	Flow $\approx 0.01 - 0.02\text{m}^3/\text{s}$ and clear
23:09	08/04/2008	0	4	-	
11:09	09/04/2008	0	1	-	
23:09	09/04/2008	0	0	-	
11:09	10/04/2008	0	1	-	Flow $\approx 0.02\text{m}^3/\text{s}$ and clear
11:18	11/04/2008	0	0	-	
11:18	12/04/2008	0	0	-	
11:18	13/04/2008	0	1	-	
11:18	14/04/2008	0	1	-	Flow $\approx 0.01 - 0.02\text{m}^3/\text{s}$ and clear
10:15	15/04/2008	0	0	-	
10:15	16/04/2008	1	0	-	Flow $\approx 0.01 - 0.02\text{m}^3/\text{s}$ and clear
10:23	17/04/2008	0	0	-	
10:23	18/04/2008	0	0	-	
10:31	19/04/2008	0	0	-	
10:31	20/04/2008	1	0	-	
10:31	21/04/2008	0	0	-	
10:31	22/04/2008	0	1	-	
10:31	23/04/2008	0	0	-	
10:31	24/04/2008	1	1	-	
10:31	25/04/2008	2	0	-	
10:31	26/04/2008	1	0	-	
10:31	27/04/2008	2	0	-	
10:31	28/04/2008	0	0	-	

Appendix D

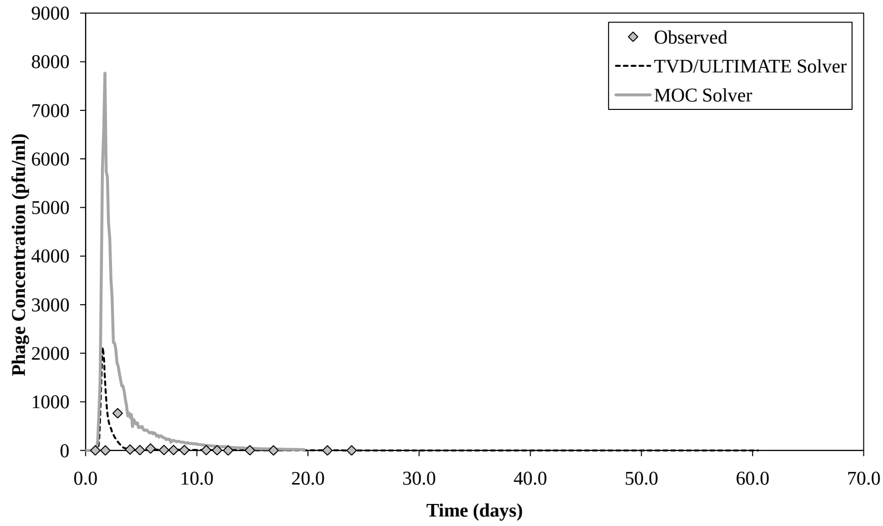
Additional Modelling Information

D.1 Selection of a solver to minimise numerical dispersion

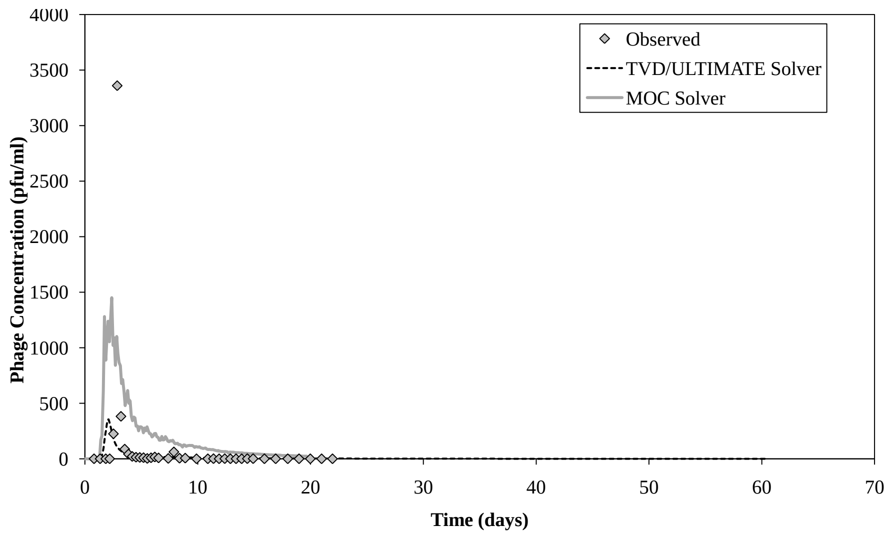
Numerical dispersion occurs as a result of the spatial discretisation (dx) of the grid. A grid dimension of 200m, with a dispersion α_x of 25m, results in a grid Peclet criterion $\alpha_x/dx = 8$. Although the TVD/ULTIMATE solver method minimises numerical dispersion due to automatic enforcement of the Courant criterion, and places some limits upon spatially introduced numerical discretisation, it is still subject to some dispersion of modelled concentration peaks (Zheng and Wang, 1999). An alternative solution method, the Method of Characteristics (MOC), virtually eliminates numerical dispersion in advection dominated problems at at the expense of introducing additional model instability, oscillations and mass balance discrepancies (Zheng and Wang, 1999). To estimate the degree and significance of numerical dispersion in the model additional simulation was carried out using the MOC solver and the results for Essendon PWS, Arkley Hole PWS and Lynchmill Spring are presented in figure D.1, the simulated peak concentrations for each solver are presented in table D.1.

For all locations the MOC solver predicts less attenuation of the tracer peaks than for the TVD/ULTIMATE method and indicates that there is some inherent numerical dispersion within the TVD/ULTIMATE solution scheme for this model and parameter set. When the global mass balance of the model is considered the MOC solver indicates nearly twice as much tracer mass is simulated by the transport model than was actually injected. A further mass discrepancy is that the total mass removed from the model to sinks such as decay, wells, drains or streams is also nearly twice that injected but is considerably greater than the modelled mass input. The TVD/ULTIMATE solver retains a relatively good mass balance to that actually injected. It is also possible that the mass discrepancy, rather than numerical dispersion could be responsible for the difference in peak concentrations.

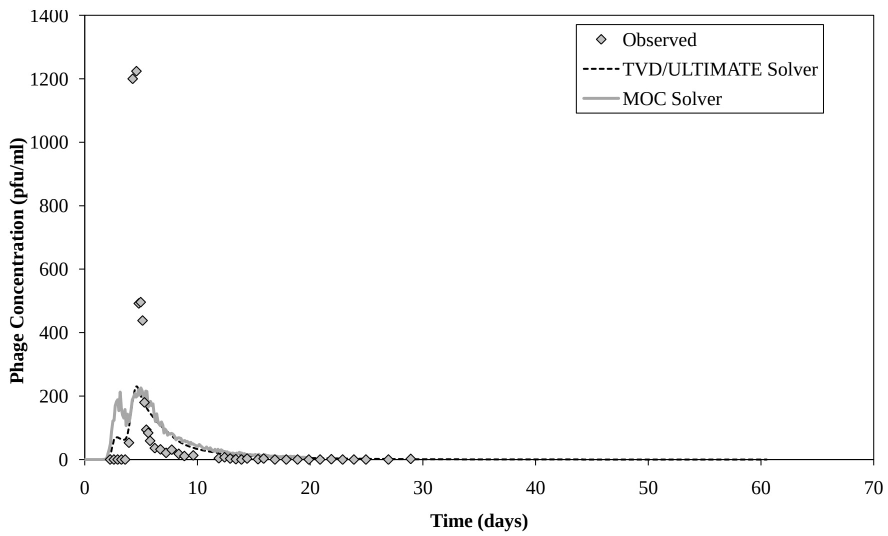
Since the error introduced by the TVD/ULTIMATE Solver relative to the MOC



(a) Essendon PWS



(b) Arkley Hole Spring



(c) Lynchmill Spring

Figure D.1: Comparison of the Method of Characteristics (MOC) Solver and the Third Order TVD/ULTIMATE Solver method for simulation of tracer breakthrough from Water End in the MT3D-MS model. Increased numerical dispersion by the TVD/ULTIMATE method is illustrated the more attenuated peaks, however oscillations in concentration are an inevitable consequence of the MOC solver.

Table D.1: Comparison of the Method of Characteristics (MOC) Solver and the Third Order TVD/ULTIMATE Solver method for simulation of *Serratia Marcescens* tracer breakthrough from Water End in the MT3D-MS model.

	Solver		
	TVD/ULTIMATE	MOC	Actual
Peak Concentrations (pfu/ml)			
Hatfield PWS	2875	11269	230
Essendon PWS	2123	7764	766
Arkley Hole	355	1451	3360
Amwell Marsh PWS	114	310	22
Rye Common PWS	199.545	279.35	3
Lynchmill Spring PWS	230.221	226	1224
Turnford PWS	22.1179	153	262
North Mymms PWS	10.4259	2766	0
Chadwell Spring	5.31626	13	0
Model Mass Balance (pfu)			
Total Input	3.34×10^{15}	5.55×10^{15}	3×10^{15}
Total Out/Decayed	3.34×10^{15}	6.19×10^{15}	3×10^{15}

solver appears to be relatively consistent, between 0.2-0.3 of the simulated peak concentration, the TVD/ULTIMATE solution is free of oscillation and retains a good mass balance, use of the TVD/ULTIMATE solver is preferred. Additionally the calibrated parameters for the TVD/ULTIMATE solver are within the range suggested by analytical modelling of the Tracer test. To utilise the MOC solver method additional calibration would be required incorporating a correct mass balance, additional mechanical dispersion and/or an increase in the dual domain mass transfer coefficient and decay constants.

A reduction in numerical dispersion and an improvement in the EPM representation could be improved through developing a finer scale refinement of the model grid, particularly in the major karst zones, although this would be at the expense of significantly increasing the computational requirements and in part the justification for deriving a sub-set model. Reducing the grid cell size would also affect the Courant Criterion, requiring a smaller time step to restrict transport to a single cell width and again increase computational requirements. Since the improvement to numerical dispersion is only marginal and the TVD/Ultimate solver provides a good limitation on time step induced numerical dispersion, changes to the model grid were not undertaken.

D.2 Alternative Representations

D.2.1 Hydraulic Conductivity Anisotropy

The introduction of a modelled karst zone an explicitly modelled EPM zone of karst is one possible representation of such a feature, an alternative model representation for this zone, and for the main karst zone is to incorporate anisotropy in hydraulic conductivity distribution between model rows and columns so as to promote pref-

Table D.2: Summary of models using an anisotropic representation of hydraulic conductivity

Model	Non karst zone	Vale of St Albans karst	Main Karst EPM	Head sum of squares	Root mean Square error
	K_y/K_x Anisotropy				
No anisotropy	1	1	1	91.00	1.7
Global anisotropy	0.9	0.9	0.9	92.8	1.8
Karst Slight	1	0.8	0.8	92.7	1.8
Karst Moderate	1	0.5	0.5	97.7	1.8
Karst strong	1	0.1	0.1	155.27	2.27

erential flow in one direction. The Hertfordshire chalk karst system has a general regional SW-NE orientation, however in practice this is comprised of several N-S and E-W aligned zones which can be aligned with model grid cells.

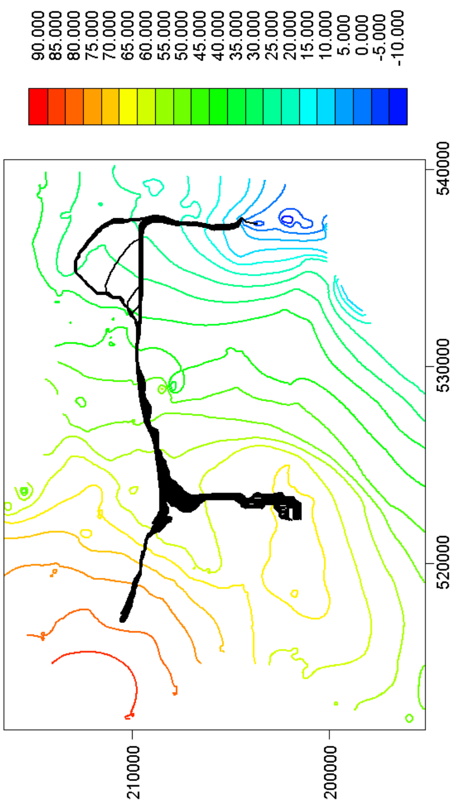
- N-S from the Mymmshall Brook to approximately the area of Hatfield
- E-W along the Palaeocene Feather edge from Hatfield to Lynchmill Spring
- N-S along the Lee Valley

An alternative groundwater flow and transport model was developed incorporating this anisotropy in horizontal hydraulic conductivity, initially as a global parameter then spatially discretised into three zones:

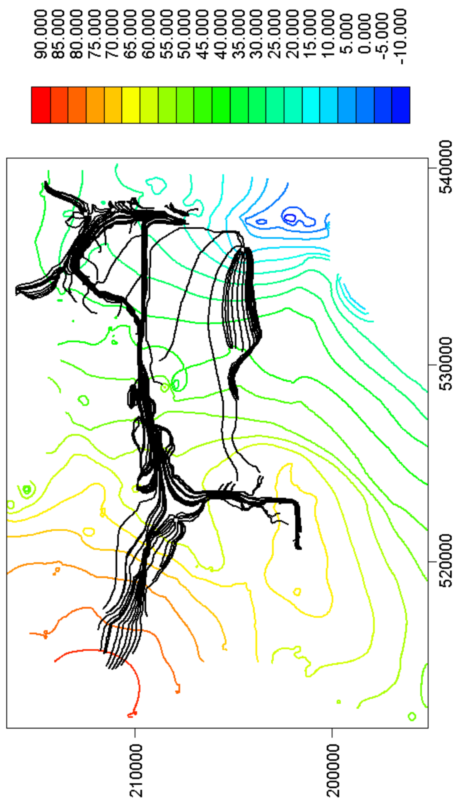
- A non karst zone comprising the majority of the model domain
- The westward karst extension of karst within the Vale of St Albans between Sandridge and Hatfield
- The main karst zone from the Mymmshall Brook area to the Lee Valley

All boundary conditions were left unchanged. Results for simulation of the tracer tests are presented in Table D.2.

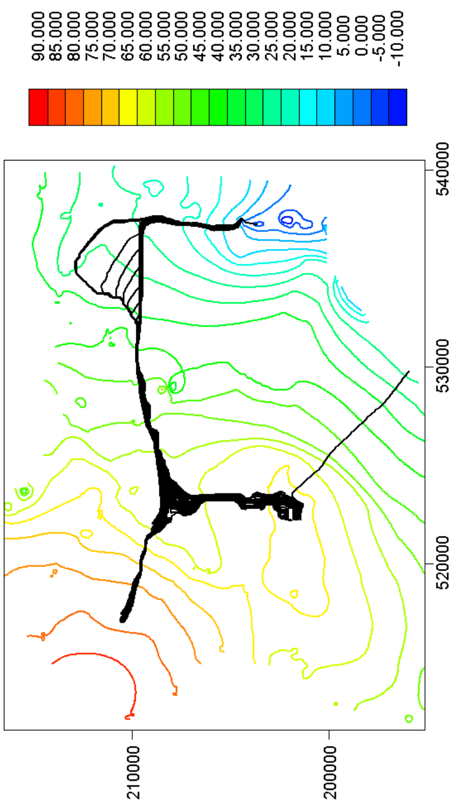
The introduction of some global or localised karstic anisotropy results in limited changes to the overall head calibration, however at increasing anisotropy deviation from observed heads increases, particularly in the North Mymms area and the Lee Valley. Both of these areas are drained by N-S aligned flow paths, increasing anisotropy along model row (approximately E-W) may restrict flow in a N-S direction and so lead to error in the head calibration (Figures D.2 and D.3). Fits to observed tracer breakthrough curves (Figure D.4) show only minor changes incorporating a small amount of anisotropy, which deviates as anisotropy increases. It may be possible to derive a new calibration incorporating anisotropy, however since the model performs and is calibrated adequately without the additional complexity introduced by anisotropy, further calibration has not been undertaken.



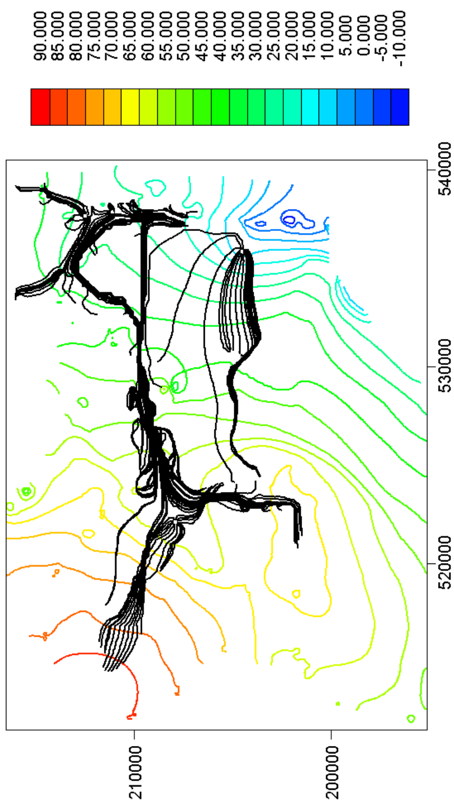
(a) $K_y/K_x = 0.9$ globally forward MODPATH



(b) $K_y/K_x = 0.9$ globally backard MODPATH

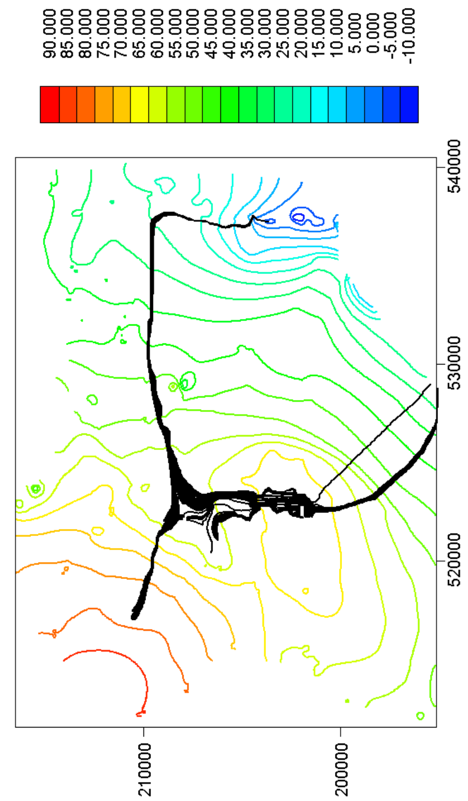


(c) $K_y/K_x = 0.8$ in karst forward MODPATH

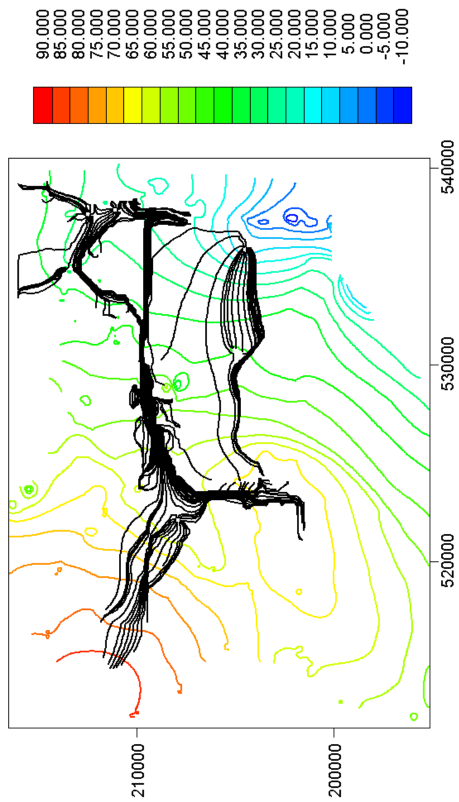


(d) $K_y/K_x = 0.8$ in karst backard MODPATH

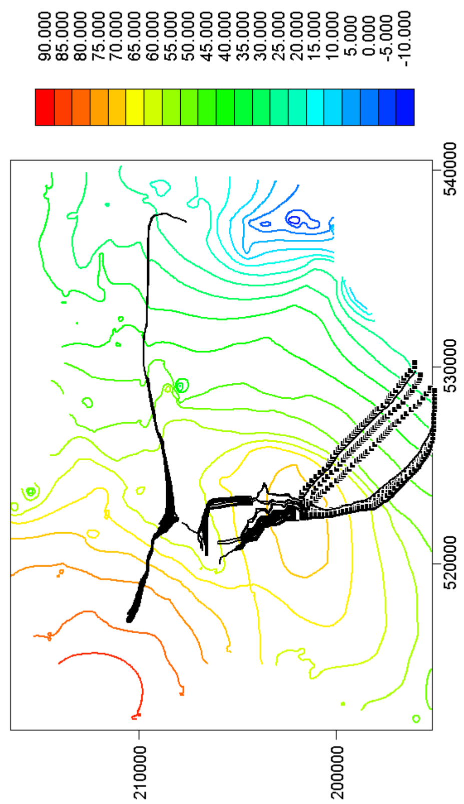
Figure D.2: Piezometry and MODPATH results for the tracer model incorporating horizontal anisotropy in the hydraulic conductivity distribution



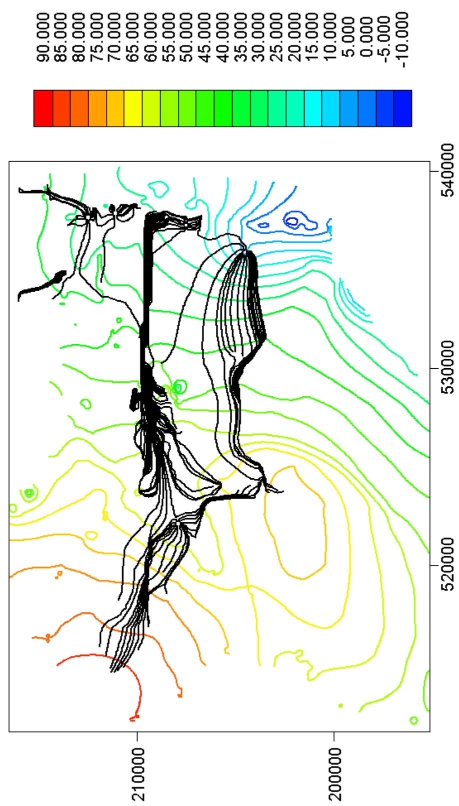
(a) $K_y/K_x = 0.5$ globally forward MODPATH



(b) $K_y/K_x = 0.5$ globally backard MODPATH

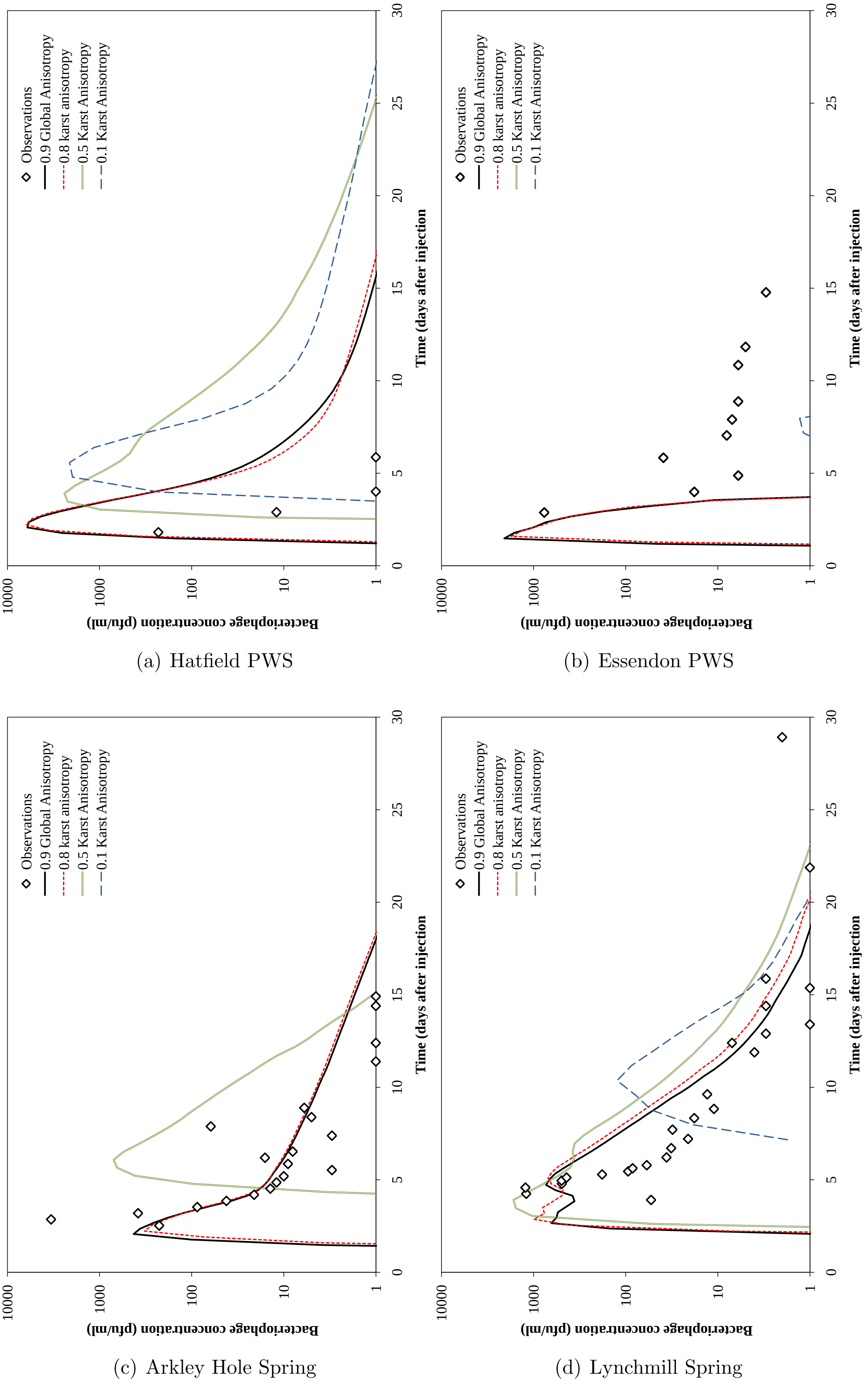


(c) $K_y/K_x = 0.1$ in karst forward MOD-PATH



(d) $K_y/K_x = 0.1$ in karst backard MODPATH

Figure D.3: Piezometry and MODPATH results for the tracer model incorporating horizontal anisotropy in the hydraulic conductivity distribution



(a) Hatfield PWS

(b) Essendon PWS

(c) Arkley Hole Spring

(d) Lynchmill Spring

Figure D.4: Simulated *Serratia Marcescens* bacteriophage breakthrough curves using the anisotropic models

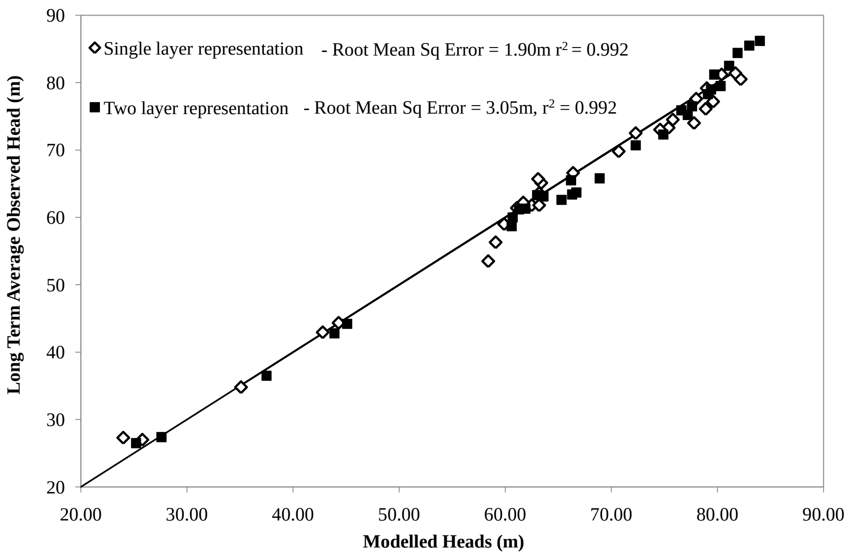


Figure D.5: Comparison of the head calibration for the vertically discretised model against that of the single layer karst model

D.2.2 Vertical Discretisation

An alternative speculated form of the Hertfordshire karst is that it is developed in a perched or semi-perched position within the zone of seasonal water table fluctuations. To investigate this, a further model representation was developed based on a two layer approach:

- The upper layer representing the zone of karst development, was essentially identical in parameterisation to the single layer karst model, however the base of the zone was arbitrarily taken to be half the original cell depth, equating to approximately 30m below the water table. On the basis of observations of karst development in the aquifer (Section 6.1.2) a clear relationship to either stratigraphy or depth cannot currently be established and therefore the base of the layer was taken to be half the effective aquifer (approximately 30m below the initial water table)

- In the lower layer of the model the high hydraulic conductivity zone representing the karst EPM was removed and was re-parameterised to values of the adjacent chalk; i.e. a hydraulic conductivity of 3m/day, effective porosity 0.01, mass transfer coefficient 1×10^{-5}.

- all other boundary conditions are unchanged

The simulation was run for steady state flow solution (Head results are shown in Figure D.5), forward and backward flowpaths (Figure D.7 and solute transport for the *Serratia Marcescens* phage (Figure D.8).

The simulated timing of peak breakthroughs to Hatfield, Essendon and Arkley Hole are approximately correct. However, the magnitude and form of the breakthrough is not well reproduced, particularly at Lee Valley locations since the ma-

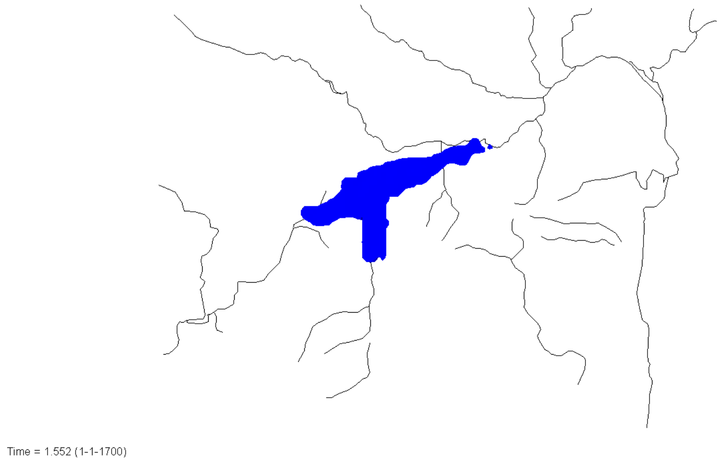
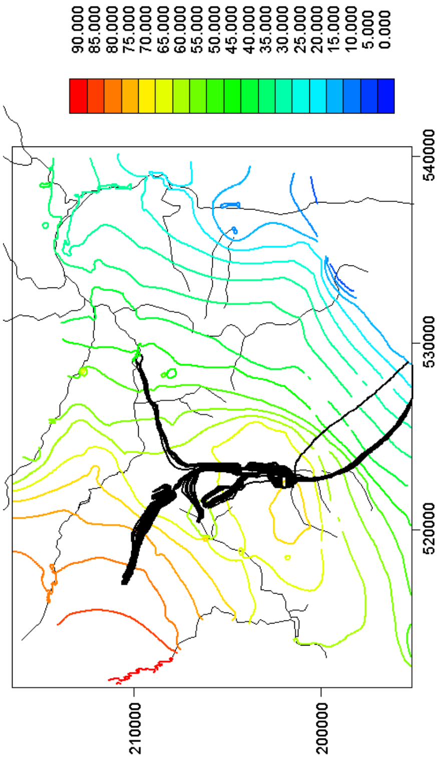
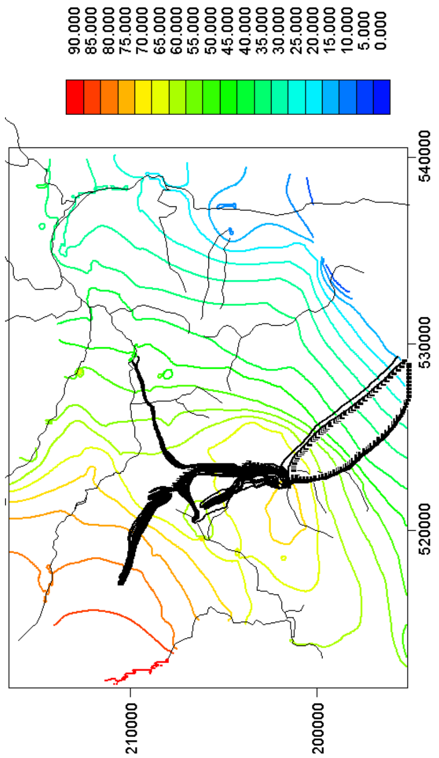


Figure D.6: Maximum extent of the *Serratia Marcescens* tracer using the vertically discretised model, the tracer does not reach beyond Arkley hole, as is also indicated by the MODPATH results

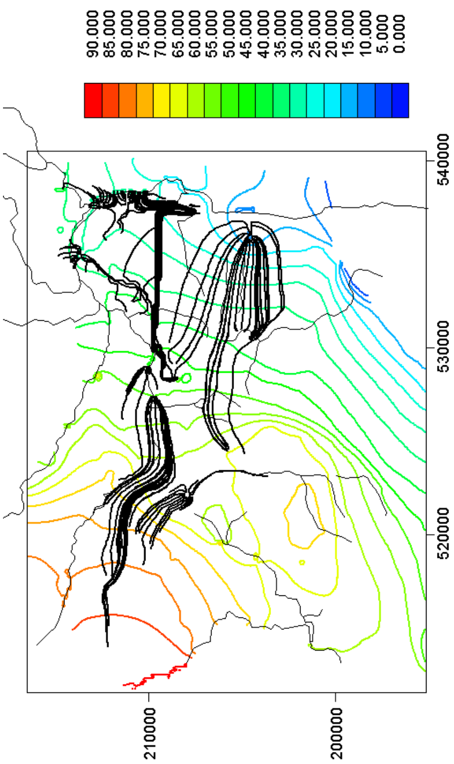
jority of tracer mass is either captured by Hatfield PWS or Tyttenhanger PWS and does not reach the Lee Valley (Figure D.6). Since no field data area available with which to validate or further calibrate a multi-layered approach in terms of heads, vertical distribution of solute and tracer transport and knowledge of aquifer properties further calibration of the multi-layered model has not been undertaken. The single layer model approach is simpler and better approximates available observations.



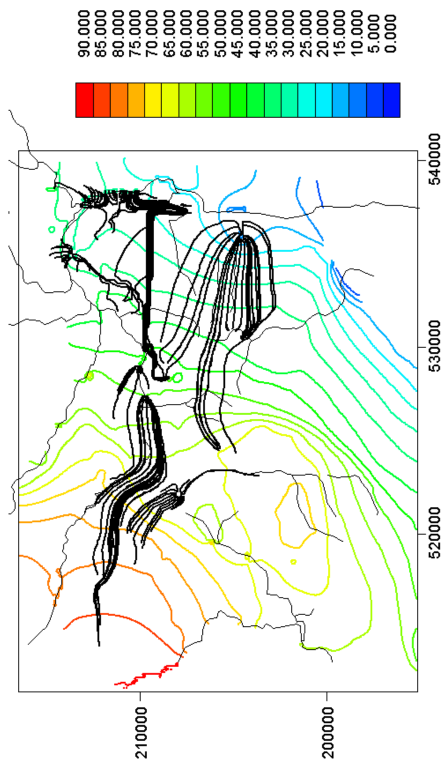
(a) Forward MODPATH pathlines and piezometric head, upper layer



(b) Forward MODPATH pathlines and piezometric head, lower layer

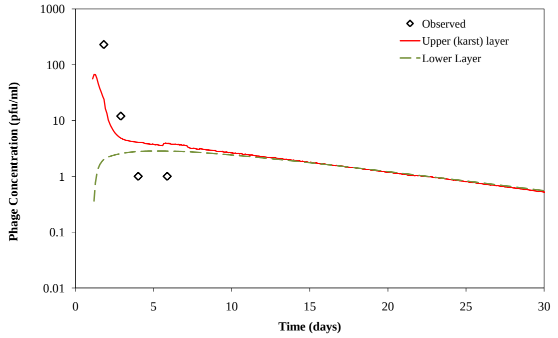


(c) Backward MODPATH pathlines and piezometric head, upper layer

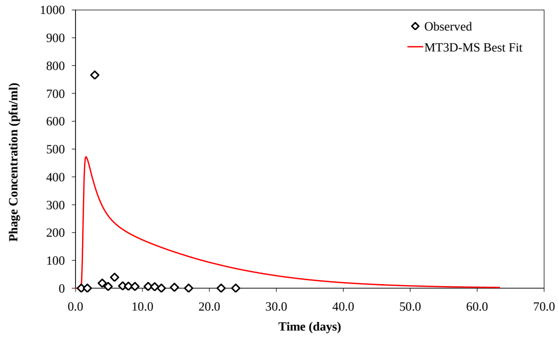


(d) Backward MODPATH pathlines and piezometric head, lower layer

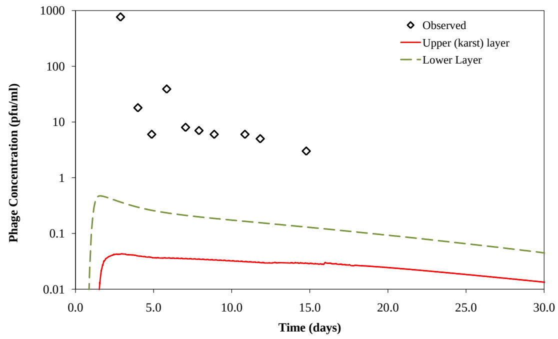
Figure D.7: Simulated MODPATH pathlines for the vertically discretised model. Since both layers are in hydraulic continuity differences in head, and therefore flow paths are limited, however velocities are significantly faster in the upper layer.



(a) Hatfield PWS



(b) Essendon PWS



(c) Arkley Hole Spring

Figure D.8: Simulated *Serratia Marcescens* bacteriophage breakthrough curves in the vertically discretised model. In the simulation the majority of tracer mass is captured either by Hatfield PWS or Tyttenhanger PWS and does not migrate to the lee valley at detectable concentrations beyond Arkley Hole

Appendix E

Fitting a CXTFIT model to Estimate the Bromate Source Term

The CXTFIT model (Toride et al., 1995) was applied in Chapter 6 to simulate the quantitative bacteriophage tracer breakthrough curves. The curve fitting abilities of the model have also been applied to simulate bromate transport using the parameters derived from both analytical and distributed finite element modelling (Table E.1).

Transport was simulated for four locations along the approximate centreline of the apparent bromate "plume"; Hatfield Quarry (WM12), Hatfield PWS, Essendon PWS and Hoddesdon PWS. The following assumptions are applied.

- All transport properties are fixed as Table E.1 except for advective velocity and dispersivity which are estimated by CXTFIT
- Initial estimates of advective velocity; 0.8m/day (From borehole dilution tracer testing) and dispersion;0.1x were adopted
- Initial estimate of the source concentration was taken as 5000μg/l for 1461 days (i.e. the NNR constant concentration source applied for 4 years)
- Bromate release is assumed to occur only as a result of the 1983-1987 recharge pulse
- Only observations made during the switch of of Hatfield PWS (2000-2005) were fit in order to eliminate the influence of Hatfield PWS scavenge pumping

The estimated source concentrations and fitted parameters are presented in Table E.2

Table E.1: Tranpsort properties adopted for the CXTFIT bromate model

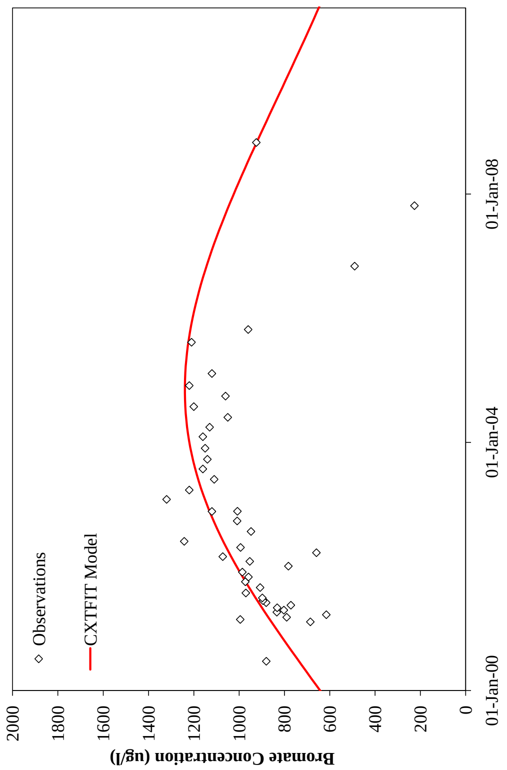
Parameter	Value adopted
Mass Transfer Coeffcient (ω)	1×10^{-6}
Proportion of Mobile Water (β)	0.94

Table E.2: Estimated parameters for the bromate CXTFIT model

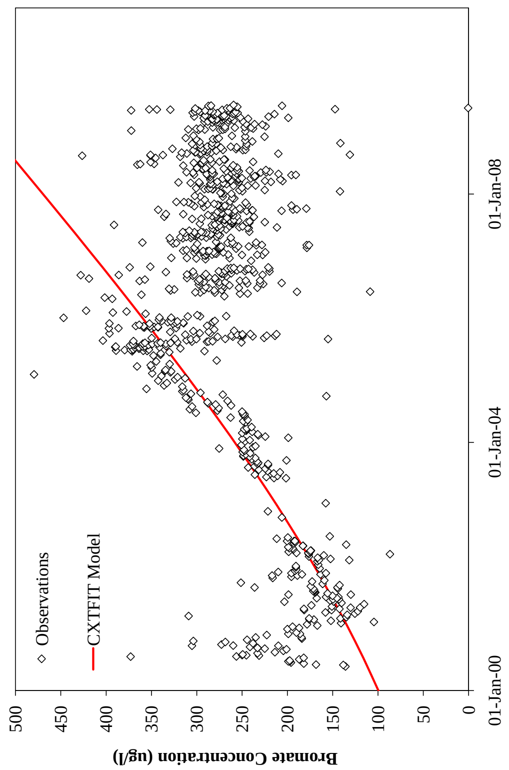
	Fitted Parameters		
	Velocity (m/day)	Dispersion	Source Concentration
Location	(m/day)	(m^2/day)	(μg/l)
Hatfield Quarry	0.28	17.63	3802
Hatfield PWS	0.15	237.8	81740
Essendon PWS	0.56	471	2402
Hoddesdon PWS	0.73	2414	6780

Note that in this case, velocity and dispersion coeffcient will represent average values for both the double porosity and conduit dominated transport along the flow path length. These models indicate using the modelled parameters, bromate concentrations on the order of a several 1000μg/l arising from leaching during the 1983-1987 site clearence can account for observed concentrations. Additionally, since these models represent only one dimensional transport, actual source concentrations may be higher.

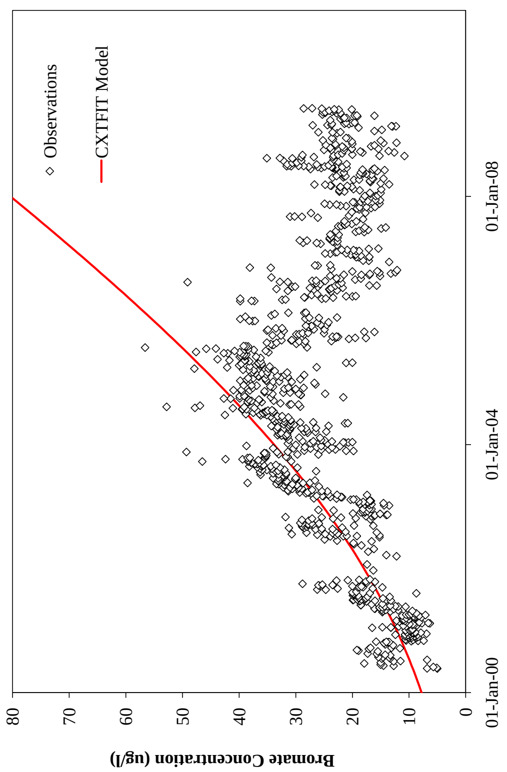
Having been fitted to observations, the models can be applied predictively. Simulated bromate transport at each location against observation is presented in Figure E.1 and E.2. Simulated concentrations indicate that with these model parameters concentrations remain at hazardous levels for many decades or even centuries. However, it should be remembered that the models are simplifications and assume that the long term rising trend from 2000-2005 is due to progressive breakthrough of a fixed concentration contaminant pulse. It does not account for changes in concentration due to abstractions or other aquifer stresses. The length of tailing of the breakthroughs are also highly sensitive to the mass transfer coeffcient adopted.



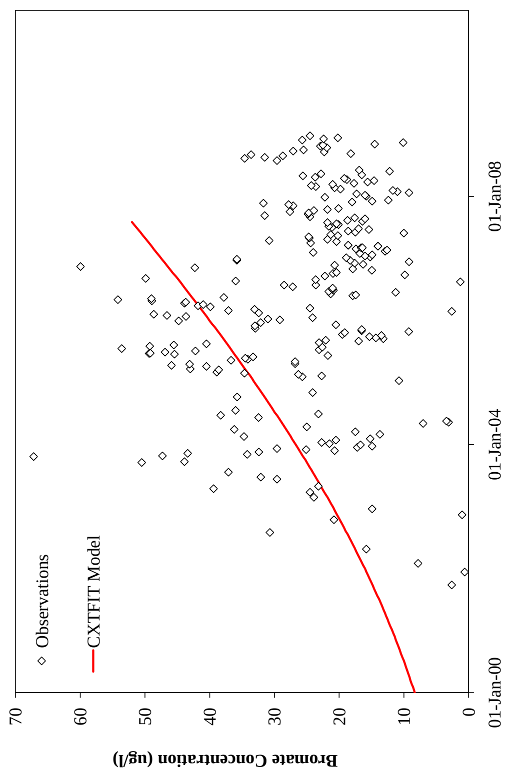
(a) Hatfield Quarry WM12



(b) Hatfield PWS

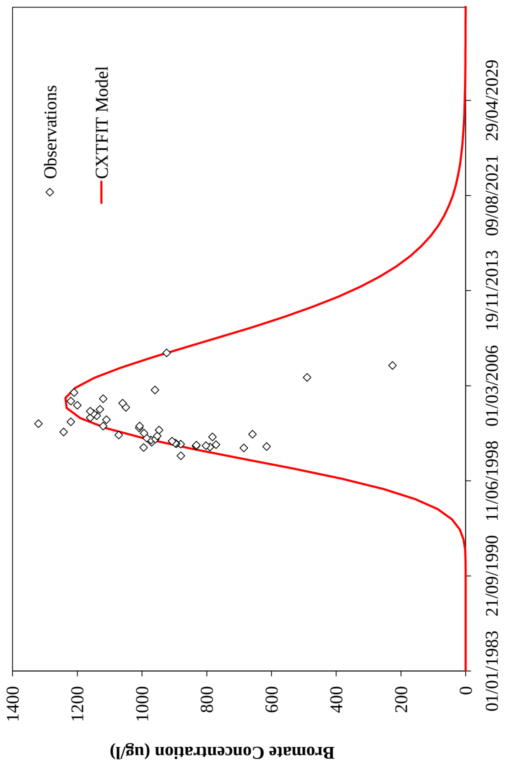


(c) Essendon PWS

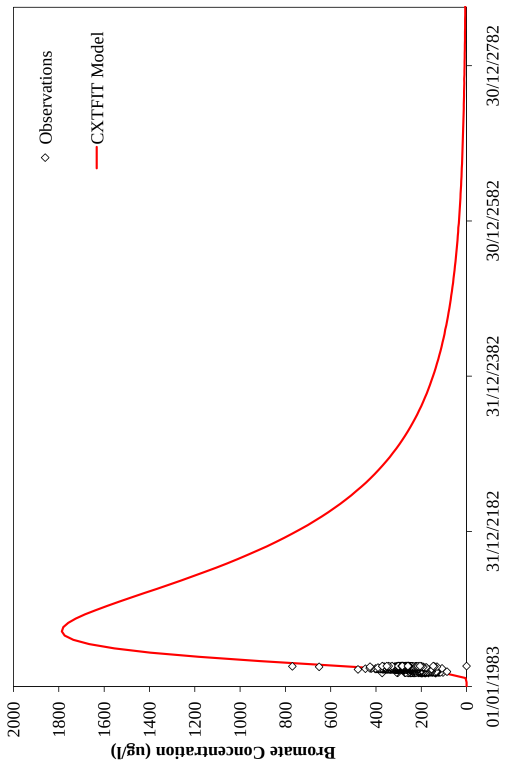


(d) Lynchmill Spring

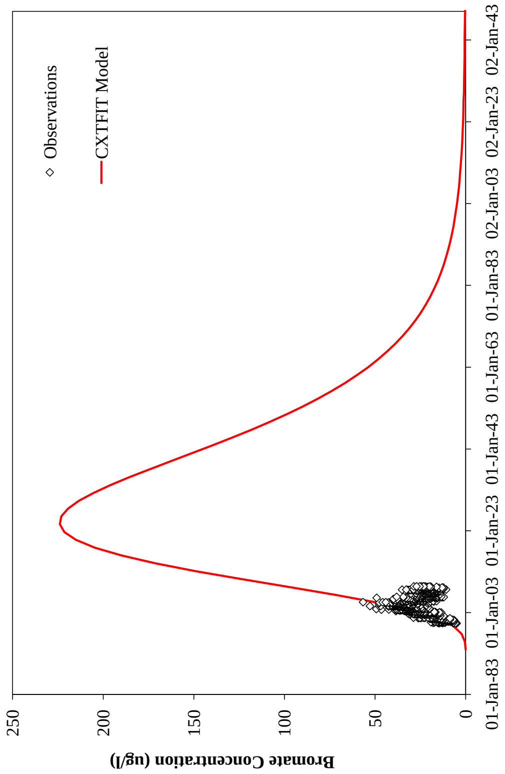
Figure E.1: Comparision of bromate simulations using CXTFIT against observations



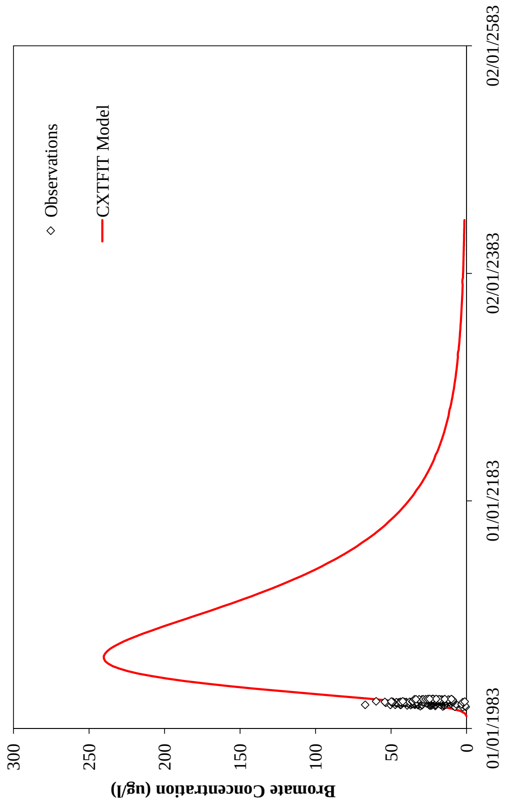
(a) Hatfield Quarry WM12



(b) Hatfield PWS



(c) Essendon PWS



(d) Lynchmill Spring

Figure E.2: Long term simulation of bromate transport using CXTFIT